

Dipolar relaxation in a many-body system of spins of 1/2

Alexander A. Nevzorov and Jack H. Freed^{a)}

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853

(Received 25 August 1999; accepted 22 October 1999)

The method utilized in Paper I [J. Chem. Phys. **112**, 1413 (2000)] for treating the density matrix equation for a two-spin system in the presence of the dipolar interaction that is randomly modulated by translational diffusion, is extended to a many-body system of identical spins of 1/2. Generalized cumulant expansions are used, which allow one to take full advantage of the statistical independence of the motions of spins. In the high-temperature approximation (appropriate for dilute solutions), for a single nonselective pulse, the symmetry of the problem allows one to obtain a compact ordered binomial expression for the free-induction decay signal that is related to the two-particle solution, and it still contains the two spin-isochromat components. The latter are evaluated by solving the corresponding stochastic Liouville equation, which allows one to recover in a unified way the two limiting cases including Anderson's result for statistical broadening in a rigid lattice and the classical Torrey-Bloembergen-Redfield expression for the motional narrowing, as corrected by Hwang and Freed. The line shape expression in the thermodynamic limit, i.e., for large numbers of particles in a macroscopic volume, is obtained. It is found that the many-body dipolar line shapes are very close to Lorentzians over the entire motional range studied, with the linewidths proportional to the spin concentration, as predicted earlier for the limiting cases. Linewidths plotted versus the values of the translational diffusion coefficient clearly show the solid-state limit, the motional-narrowing limit, and the intermediate region. The method is extended to describe the behavior of the many-body system in a solid-echo sequence. This enables one to obtain the homogeneous T_2 's over the whole range of motions. A minimum in T_2 is found at approximately the same value of translational diffusion coefficient as was found for the two-spin case in Paper I.

© 2000 American Institute of Physics. [S0021-9606(00)02903-2]

I. INTRODUCTION

The problem of the description of spectral line shapes in the presence of dipolar interaction amongst a collection of spins is well known in magnetic resonance spectroscopy. Since there is an r^{-3} dependence of the magnitude of the dipolar coupling on r , the vector connecting any two spins, the calculation of spectral line shapes in such spin systems is essentially a many-body problem. Indeed, if only a selected pair of spins were considered, the equilibrium probability density for the distribution in r would be inversely proportional to the sample volume V , thus yielding a negligible effect of the dipolar interaction on spectral line shapes for macroscopic V . Our goal, therefore, is to consider all the spins as a single many-body system and to find the thermodynamic limit for the spectral line shape as the number of spins $N \rightarrow \infty$, while at the same time $V \rightarrow \infty$. In earlier work by Torrey, under conditions of motional narrowing, the effect of multiple spins was treated by first solving the two-spin problem and then introducing in *ad hoc* fashion the concentration factor rendering the many-body interaction as a sum of N two-body interactions for the $N+1$ th particle.¹⁻³ This yielded Lorentzian line shapes with the spin-lattice, $R_1 \equiv T_1^{-1}$, and transverse, $R_2 \equiv T_2^{-1}$, relaxation rates which depend linearly on concentration. In solids, magnetic resonance line shapes can be calculated using the statistical

theory of Anderson,^{4,5} which also yields simple Lorentzians over a broad frequency range. However, in the latter case the spectra are inhomogeneously broadened.

In this paper we examine more rigorously the many-body effects on spectral line shapes and observed time-resolved signals. The emphasis is placed on spin relaxation by translational diffusion, which modulates the dipolar interactions between spins. Our general method yields a soluble stochastic Liouville equation procedure for the many-body problem in the thermodynamic limit, which allows one to calculate spectra over the whole motional regime and to recover both the solid-state limit and the motional narrowing regime as limiting cases. Our procedure may be summarized as follows. In Sec. II, we expand the density matrix in a set of eigenoperators of the unperturbed Hamiltonian (cf. Paper I, i.e., Ref. 6), which enables us to conveniently separate the quantum spin variables from the classical stochastic variables, i.e., r_{ij} $i, j = 1, \dots, N$ in the N -spin case. Then we obtain a system of coupled differential equations for the expansion coefficients, the solution of which can be written in terms of an ordered exponential. In Sec. III, we show that the ensemble-average of the latter can be written in terms of connected averages, or cumulants,⁷⁻⁹ which allows one to find the solution for the observed magnetic resonance signal in terms of a time-ordered binomial sum of the two spin isochromats related to the solution of the two-body problem. Finally, in Sec. IV the Markov method¹⁰ is used to find the thermodynamic limit for the line shape expression when N

^{a)}Electronic mail: jfh@msc.cornell.edu

$\rightarrow\infty$, $V\rightarrow\infty$. This leads to an integral equation for the many-body signal in terms of the two-spin signal, that was calculated in Paper I.⁶ The integral equation is then solved by straightforward numerical methods, (cf. Sec. IV), and the continuous-wave (cw) line shapes are described in Sec. VII. In this work we use the high-temperature approximation to lowest order and do not consider any higher-order effects of the sort studied elsewhere.^{11,12} This may also be taken as implying dilute solutions. Here we show that the cw line shape is a Lorentzian over the whole motional range. We also show rigorously that the linewidth is linearly proportional to the concentration of spins in the sample over the whole motional range.

The methodology is generalized to the solid-echo experiment in Secs. V and VI. In Sec. VII we investigate how motion quenches the echo formation. By simulating the SECSY (spin-echo correlation spectroscopy) spectra based on the solid echo, we are able to decompose the total Lorentzian linewidths into their homogeneous and inhomogeneous components. In addition, we show how increasing concentration quenches the echo even when there is almost no appreciable motion because of the fractional power-law dependence of the homogeneous T_2 on the motional rate. This effect is distinct from instantaneous diffusion⁴ which reflects the fact that a standard π pulse will not refocus dipolar interactions between like spins.

II. COUPLING OF THE FREE-INDUCTION DECAY COMPONENTS WITHIN THE EIGENOPERATOR BASIS

Here we consider a system of N particles of spins $1/2$ which diffuse in a sample of volume V . The Hamiltonian for such a system in the rotating frame can be written as

$$H_R = H_{0,R} + \sum_{i < j}^N H^{(ij)}. \quad (2.1)$$

Here the double sum is taken over all N spins i and j forming distinct pairs such that $i < j$. For like spins the unperturbed Zeeman Hamiltonian $H_{0,R}$ is given by

$$H_{0,R} = \sum_{i=1}^N (\Omega_i - \omega_{rf}) I_z^{(i)} = \Delta\Omega \sum_{i=1}^N I_z^{(i)}. \quad (2.2)$$

Here we consider the high-field approximation and retain only the first term of the dipolar Hamiltonian, namely

$$H_R^{(ij)} = H^{(ij)} = \chi \frac{Y_0^{(2)}(\Omega_{ij})}{r_{ij}^3} [I_z^{(i)} I_z^{(j)} - \frac{1}{4}(I_+^{(i)} I_-^{(j)} + I_-^{(i)} I_+^{(j)})], \quad (2.3)$$

where $\chi = \sqrt{16\pi/5} \gamma^2 \hbar$ is the coupling constant, r_{ij} is the distance between the i th and j th spins, Ω_{ij} is the orientation of the vector \mathbf{r}_{ij} connecting the two spins with respect to the main magnetic field. If r_{ij} and/or Ω_{ij} are random functions of time, the dipolar interaction gives rise to line broadening. The equation of motion for the many-body density matrix is

$$\frac{\partial \rho(t)}{\partial t} = -i[H_0, \rho(t)] - i \sum_{i < j}^N [H^{(ij)}, \rho(t)]. \quad (2.4)$$

It should be noted that the density matrix contains both explicit and implicit time dependence, the latter arising from stochastic modulation through the vectors \mathbf{r}_{ij} . We seek the solution of the density matrix equation in the form

$$\rho(t) = \sum_{\{\epsilon\}} g_{\{\epsilon\}}(t) E_{\{\epsilon\}}, \quad (2.5)$$

where the coefficients $g_{\{\epsilon\}}(t)$ are functions of time, and the $E_{\{\epsilon\}}$ are a set of basis operators with numbering scheme $\{\epsilon\}$, that are introduced as follows. For a system of N particles of spin $1/2$, operators $E_{\{\epsilon\}}$ can be written as a direct product of N spin operators corresponding to different particles¹³

$$E_{\{\epsilon\}} = \prod_{i=1}^N I_{\epsilon_i}^{(i)}. \quad (2.6)$$

Here $\{\epsilon\}$ denotes a permutation set which provides a certain numbering prescription for the eigenoperators, $\{\epsilon\} = \{\epsilon_1, \epsilon_2, \dots, \epsilon_N\}$, $\epsilon_i = \alpha, \beta, +, \text{ or } -$. I_+ and I_- are conventional raising and lowering spin operators and the polarization operators I_α and I_β are defined as Ref. 14, cf. Paper I

$$I_\alpha = \frac{1}{2} I_z, \quad I_\beta = \frac{1}{2} - I_z. \quad (2.7)$$

As follows from the trace properties of I_+ , I_- , I_α , and I_β , the operators of Eq. (2.6) form a complete orthonormal basis set in operator space with the Frobenius trace metric defined as

$$(E_{\{\epsilon\}}, E_{\{\epsilon'\}}) \equiv \text{Tr}(E_{\{\epsilon\}}^\dagger E_{\{\epsilon'\}}) = \delta_{\{\epsilon\}, \{\epsilon'\}}, \quad (2.8)$$

where the dagger \dagger denotes the Hermitian conjugate. By using the above orthogonality property of the basis operators, one obtains a system of equations which couple the FID (free induction decay) components $g_{\{\epsilon\}}(t)$. That is

$$\frac{\partial g_{\{\epsilon\}}(t)}{\partial t} = -i\Delta\Omega_{\{\epsilon\}} g_{\{\epsilon\}}(t) - i\chi \sum_{i < j}^N C_{\{\epsilon\}\{\epsilon'\}}^{(ij)} F(\mathbf{r}_{ij}) g_{\{\epsilon'\}}(t). \quad (2.9)$$

The matrix of frequency offsets is given by $[H_0, E_{\{\epsilon\}}] = \Delta\Omega_{\{\epsilon\}} E_{\{\epsilon\}}$, and the matrix $\mathbf{C}^{(ij)}$ is defined by

$$\chi C_{\{\epsilon\}\{\epsilon'\}}^{(ij)} F(\mathbf{r}_{ij}) = \text{Tr}(E_{\{\epsilon\}}^\dagger [H^{(ij)}, E_{\{\epsilon'\}}]). \quad (2.10)$$

The explicit form of $\mathbf{C}^{(i,j)}$ clearly depends on the commutation relations between the basis operators and the Hamiltonian describing the interaction among the spin particles. In the case of the dipolar interaction in the high-field approximation; Eq. (2.3), one obtains the following commutation properties for different types of pairwise combinations $I_{\epsilon_i}^{(i)} I_{\epsilon_j}^{(j)}$:

$$\begin{aligned} [H^{(ij)}, I_\alpha^{(i)} I_\alpha^{(j)}] &= [H^{(ij)}, I_\beta^{(i)} I_\beta^{(j)}] \\ &= [H^{(ij)}, I_+^{(i)} I_+^{(j)}] \\ &= [H^{(ij)}, I_-^{(i)} I_-^{(j)}] = 0, \\ [H^{(ij)}, I_\pm^{(i)} I_\alpha^{(j)}] &= \pm \chi F(\mathbf{r}_{ij}) (\frac{1}{2} I_\pm^{(i)} I_\alpha^{(j)} + \frac{1}{4} I_\alpha^{(i)} I_\pm^{(j)}), \\ [H^{(ij)}, I_\pm^{(i)} I_\beta^{(j)}] &= \mp \chi F(\mathbf{r}_{ij}) (\frac{1}{2} I_\pm^{(i)} I_\beta^{(j)} + \frac{1}{4} I_\beta^{(i)} I_\pm^{(j)}), \\ [H^{(ij)}, I_\alpha^{(i)} I_\beta^{(j)}] &= \chi F(\mathbf{r}_{ij}) (\frac{1}{4} I_+^{(i)} I_-^{(j)} - \frac{1}{4} I_-^{(i)} I_+^{(j)}), \\ [H^{(ij)}, I_+^{(i)} I_-^{(j)}] &= \chi F(\mathbf{r}_{ij}) (\frac{1}{4} I_\alpha^{(i)} I_\beta^{(j)} - \frac{1}{4} I_\beta^{(i)} I_\alpha^{(j)}), \end{aligned} \quad (2.11)$$

where $F(\mathbf{r}_{ij}) \equiv Y_0^{(2)}(\Omega_{ij})/r_{ij}^3$. Thus in the case of the Hamiltonian given by Eq. (2.3), the matrices $\mathbf{C}^{(i,j)}$ are real and symmetric. Out of the possible 4^N time-dependent coefficients $g_{\{\epsilon\}}(t)$ of Eq. (2.5), most do not contribute to the observable signal. Indeed, the observable free induction decay (FID) signal can be written as

$$G(t) = \text{Tr} \left(\rho \sum_{i=1}^N I_-^{(i)} \right) = \sum_{\{\epsilon\}} g_{\{\epsilon\}}(t) \sum_{i=1}^N \text{Tr}(E_{\{\epsilon\}} I_-^{(i)}). \quad (2.12)$$

Therefore, a nonzero contribution to the observed signal arises from the coefficients $g_{\{\epsilon\}}(t)$ corresponding to the operators $E_{\{\epsilon\}}$ that contain *only one* operator I_+ and a mixture of polarization operators I_α and I_β . Others will yield a zero trace upon multiplication by an I_- . Moreover, as can be seen from the commutation properties, they will be coupled via $H^{(ij)}$ to those coefficients which correspond to operators having the total number of operators I_+ that exceeds the number of operators I_- by +1. The difference between the number of operators I_+ and I_- in an eigenoperator $E_{\{\epsilon\}}$ we shall call the *coherence index* μ , $[H_0, E_{\{\epsilon\}}^\mu] = \mu \Delta \Omega E_{\{\epsilon\}}^\mu$. Thus, in calculating a pure FID signal only the components corresponding to $\mu = +1$ are important, (the counter-rotating component corresponding to $\mu = -1$ is related to it by complex conjugation, cf. Paper I). We, therefore, rearrange the set $\{\epsilon\}$ into four subsets, and we introduce the following nomenclature for the operators $E_{\{\epsilon\}}$ with $\mu = 1$ that are necessary to calculate the observed FID signal, Eq. (2.12), from Eq. (2.9):

$$\begin{aligned} E_{\{\epsilon\}} &\equiv E_{\{\epsilon\}}^{(k,m)} = E_{\{i\}_\alpha \{i'\}_\beta \{i''\}_+ \{i'''\}_-}^{(k,m)} \\ &= I_\alpha^{(i_1)} I_\alpha^{(i_2)} \dots I_\alpha^{(i_m)} I_\beta^{(i'_1)} I_\beta^{(i'_2)} \dots I_\beta^{(i'_{m'})} I_+^{(i''_1)} I_+^{(i''_2)} \dots \\ &\quad I_+^{(i''_{k+1})} I_-^{(i'''_1)} I_-^{(i'''_2)} \dots I_-^{(i'''_k)}, \end{aligned} \quad (2.13)$$

where $m + m' + 2k + 1 = N$, m denotes the number of operators I_α , k is the number of pairs $I_+ I_-$, set $\{i\}_\alpha$ denotes all the possible choices of m particles out of a total N for m operators I_α , and so on. Two indices k and m are sufficient for the classification of the basis operators $E_{\{\epsilon\}}^{(k,m)}$ and for the establishment of the general character of couplings amongst the corresponding coefficients $g_{\{\epsilon\}}^{(k,m)}(t)$. Strictly speaking, one should also have an additional index μ corresponding to the coherence index of the eigenoperator. However, since only the eigenoperators having $\mu = +1$ are important for calculating the FID signal, this index is omitted here. The number of such operators with given k and m is

$$\frac{N!}{N_\alpha! N_\beta! N_+! N_-!} = \frac{N!}{m!(N-2k-m-1)!(k+1)!k!}. \quad (2.14)$$

And the total number of operators $E_{\{\epsilon\}}^{(k,m)}$ having $\mu = +1$ for N particles of spin 1/2 is given by

$$\begin{aligned} 2^{N-\mu} \sum_{k=0}^{[N-\mu/2]} \binom{N}{2k+\mu} \binom{2k+\mu}{k} 2^{-2k} \\ = \binom{2N}{N+\mu} \bigg|_{\mu=1} = \binom{2N}{N+1}, \end{aligned} \quad (2.15)$$

which can be proved by induction with respect to N . In terms of the above nomenclature the expression for the FID, Eq. (2.12), becomes

$$G(t) = \sum_{m=0}^{N-1} \sum_{\{\epsilon\}} g_{\{\epsilon\}}^{(0,m)}(t). \quad (2.16)$$

As one can see from the commutation relations, Eq. (2.11), the mixture of α , β , $+$, and $-$ terms gives rise to the coupling amongst the coefficients $g_{\{\epsilon\}}^{(k,m)}(t)$ and $g_{\{\epsilon'\}}^{(k',m'\pm 1)}(t)$, that is amongst those that have the same value of $l \equiv k + m$. Therefore, one can rewrite Eq. (2.9) for the separate FID components $g_{\{\epsilon\}}^{(k,m)}(t)$ as the following block-matrix diagram:

$$\frac{\partial \mathbf{g}(t)}{\partial t} = \begin{array}{c} \begin{array}{c} (k, m) \\ \begin{array}{c} \boxed{(0, N-1)} \\ \boxed{(0, N-2)} \\ \boxed{(1, N-3)} \\ \boxed{(0, N-3)} \\ \boxed{(1, N-4)} \\ \boxed{(2, N-5)} \\ \vdots \\ \boxed{(0, 0)} \end{array} \end{array} \begin{array}{c} l = k + m = N - 1 \\ \\ l = N - 2 \\ \\ l = N - 3 \\ \\ \vdots \\ l = 0 \end{array} \left\{ \begin{array}{l} \{I_\alpha I_\alpha I_\alpha \dots I_\alpha\} \\ \{I_\alpha I_\alpha I_\alpha \dots I_\alpha I_\beta\} \\ \{I_\alpha I_\alpha I_\alpha \dots I_\alpha I_+\} \\ \{I_\alpha I_\alpha \dots I_\alpha I_\beta I_\alpha I_\beta\} \\ \{I_\alpha I_\alpha \dots I_\alpha I_\beta I_+\} \\ \{I_\alpha I_\alpha \dots I_\alpha I_\beta I_\beta I_+\} \\ \vdots \\ \{I_\alpha I_\beta \dots I_\beta I_\beta I_\beta I_+\} \end{array} \right\} \times \mathbf{g}(t) \end{array} \quad (2.17)$$

which describes the time evolution of the overall vector of coefficients $\mathbf{g}(t)$. In Eq. (2.17) we have rearranged the total vector $\mathbf{g}(t)$ into N parts or sub-vectors, $\mathbf{g}_l(t)$, $l = 0, 1, \dots, N-1$, that decouple from each other, so we can consider them separately. Note that only the components that correspond to the shaded areas (i.e., with $k=0$) contribute to the observable FID signal.

III. ENSEMBLE-AVERAGED SOLUTION USING THE GENERALIZED CUMULANTS

For the case of like spins, $\Delta \Omega_{\{\epsilon\}} = \Delta \Omega$ for all $\{\epsilon\}$, one can eliminate the first term on the right-hand side of Eq. (2.9) by performing the transformation into the interaction representation

$$g_{\{\epsilon\}}^{(k,m)}(t) \rightarrow \hat{g}_{\{\epsilon\}}^{(k,m)}(t) e^{-i \Delta \Omega t}. \quad (3.1)$$

Below we shall solve for the $\hat{g}_{\{\epsilon\}}^{(k,m)}(t)$, but we shall drop the carat symbol for simplicity in notation. One is in fact interested in an ensemble-averaged solution for the overall vector of coefficients, $\mathbf{g}(t)$, which is given by an ordered matrix exponential for each of its decoupled subvectors $\mathbf{g}_l(t)$

$$\mathbf{g}_l(t) = \left\langle \exp_O \left[-i \chi \sum_{i_1 < j_1}^N C_{i_1 j_1}^{(i_1 j_1)} \int_0^t dt_1 F(\mathbf{r}_{i_1 j_1}(t_1)) \right] \right\rangle \mathbf{g}_l(0). \quad (3.2)$$

$$G(t) = 2^{-N} qN \exp(-i\Delta\Omega t) O \left\{ \exp_O \left[\sum_{n=1}^{\infty} (i\frac{3}{4}\chi)^n K_n(t) \right] + \exp_O \left[\sum_{n=1}^{\infty} (-i\frac{3}{4}\chi)^n K_n(t) \right] \right\}^{N-1}. \quad (3.11)$$

Equation (3.11) is a remarkable result, which means that the FID for N particles of spins $1/2$ can be simply written as a time-ordered binomial sum of $(N-1)$ th degree of the corresponding ensemble-averaged spin isochromats from a single pair of particles [compare Eq. (3.11) to Eq. (2.14) of Paper I]. The only assumption that has been made is that the motions of all particles are stochastically independent. In fact, in deriving Eq. (3.11) we did not even assume any specific form for the $F(\mathbf{r}(t))$ or the detailed nature of the stochastic process responsible for its modulation. In treating the quantum-mechanical spin variables the only requirements were: (i) Identical spins of $1/2$ and (ii) a purely secular form for the spin Hamiltonian of Eq. (2.1). The particular form of the spin-part of Eq. (2.3), relevant for the dipolar interactions, merely determined the eigenvalue of $3/4$ that shows up in Eq. (3.11).

To recover the motional narrowing regime as a limiting case, one can truncate the cumulant expansion of the exponential in Eq. (3.11) at the second order. Assuming for simplicity that the system is on resonance, $\Delta\Omega=0$, and that $\langle F(\mathbf{r}(t)) \rangle = 0$, this yields the well-known result^{2,15}

$$\begin{aligned} G(t) &= \frac{qN}{2} O \exp_O \left[-(N-1) \right. \\ &\quad \times \frac{9}{16} \chi^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \langle F(\mathbf{r}(t_1)) F(\mathbf{r}(t_2)) \rangle_c \Big] \\ &= \frac{qN}{2} \exp \left[-(N-1) \frac{9}{16} \chi^2 \int_0^{t \rightarrow \infty} d\tau (t-\tau) \right. \\ &\quad \times \langle F(\mathbf{r}(0)) F(\mathbf{r}(\tau)) \rangle \Big] \\ &= \frac{qN}{2} \exp \left[-(N-1) \frac{9}{32} \chi^2 J(0) t \right], \end{aligned} \quad (3.12)$$

where $J(0) = 2 \int_0^\infty d\tau \langle F(\mathbf{r}(0)) F(\mathbf{r}(\tau)) \rangle$ is the zero-frequency spectral density for translational diffusion. The explicit analytical expression for $J(0)$ has been calculated by Torrey,¹ and corrected later by Hwang and Freed³ who have treated the excluded volume more rigorously. For the translational diffusion with coefficient D_T and the distance of minimum approach d , the simplified treatment yields: $J(0) = (2/15) \times (1/V) (2/dD_T)$, cf. Eq. (114'), p. 302 of Ref. 2. In the more rigorous treatment, the coefficient $2/15$ should be replaced³ by $4/27$. Here we have explicitly included the sample volume, V , which arises from the averaging of the two-particle correlation function of Eq. (3.12) with respect to the equilibrium probability density. Also, we have defined D_T as the relative diffusion coefficient. When D_T is replaced by $2D$, where D is the diffusion coefficient for individual particles, then the original formula of Ref. 2 is recovered. This shows rigorously that under the conditions of motional narrowing,

the FID signal from N identical spins of $1/2$ is given by a single exponential, the decay of which is simply proportional to the concentration of spins, C , in the sample, and the intensity is proportional to the number of spins, N .

Another important special case is when motions become very slow. In this case the cumulant expansion of the ensemble averaged exponentials, Eq. (3.11), can be rewritten as ordinary exponentials, oscillating with a constant frequency $3/4 \chi F(\mathbf{r})$, which are integrated over \mathbf{r} . That is

$$\begin{aligned} &\exp_O \left[\sum_{n=1}^{\infty} \left(\pm i \frac{3}{4} \chi \right)^n K_n(t) \right] \\ &= \left\langle \exp_O \left[\pm i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle \\ &= \int \frac{d^3\mathbf{r}}{V} \exp[\pm i \frac{3}{4} \chi F(\mathbf{r}) t]. \end{aligned} \quad (3.13)$$

The resulting FID signal can then be written as

$$G(t) = 2^{-N} qN \left\{ \int \frac{d^3\mathbf{r}}{V} [e^{-i(3/4)\chi F(\mathbf{r})t} + e^{i(3/4)\chi F(\mathbf{r})t}] \right\}^{N-1}. \quad (3.14)$$

One can evaluate Eq. (3.14) in the thermodynamic limit, $N \rightarrow \infty$ and $V \rightarrow \infty$, by rewriting it as

$$\begin{aligned} G(t) &\propto \lim_{N \rightarrow \infty} \frac{qN}{2} \left\{ 1 - \frac{C}{2N} 2\pi \int \sin \theta d\theta \int_{-\infty}^{+\infty} r^2 dr \right. \\ &\quad \times [1 - e^{i(3/4)\chi F(\mathbf{r})t}] \Big\}^{N-1}, \end{aligned} \quad (3.15)$$

so that the concentration of spins $C = N/V$ is kept constant. Calculation of Eq. (3.15) yields a single exponential with a decay rate of $(2\pi^2/3\sqrt{3})\gamma^2\hbar C$, which constitutes the well-known Anderson result.^{2,4,16}

IV. THERMODYNAMIC LIMIT OF THE MANY-BODY LINE SHAPE AS $N \rightarrow \infty$, $V \rightarrow \infty$

Equation (3.11) can be evaluated in the limiting case of an infinite number of particles in a manner analogous to the Markov method used in the ESR of solids.¹⁷ For simplicity we shall assume that the system is on resonance, $\Delta\Omega=0$, and rewrite the cumulant expansions, Eq. (3.11), in terms of ensemble-averaged ordered exponentials using the first equality in Eq. (3.13)

$$\begin{aligned} G(t) &= (2^{-N} qN) O \left\{ \left\langle \exp_O \left[-i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle \right. \\ &\quad \left. + \left\langle \exp_O \left[i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle \right\}^{N-1}. \end{aligned} \quad (4.1)$$

Letting $N=2$ we recover the FID signal from a single pair of particles which consists of two-spin isochromats, cf. Eq. (2.14) of Paper I. If not for the ordering O in front of the binomial expression, Eq. (4.1), the functions $\langle \exp_O[\mp i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t'))] \rangle$ could be immediately evaluated by solving the corresponding stochastic Liouville equation as described in Paper I. However, for the case of a very large number of particles the obstacle of having this additional ordering can be eliminated. For this purpose, we shall find the statistical limit for Eq. (4.1) at $N \rightarrow \infty$ while at the same time $V \rightarrow \infty$. As will shortly be seen, the limit $V \rightarrow \infty$ can be treated by introducing a slightly different notation for an ensemble average.

The ordered exponentials are averaged by means of joint probability densities. For example, for a stationary Markov process, the joint probability density is given by:

$$p_n(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2; \dots; \mathbf{r}_n, t_n) \\ = P(\mathbf{r}_1, t_1 | \mathbf{r}_2, t_2) \cdots P(\mathbf{r}_{n-1}, t_{n-1} | \mathbf{r}_n, t_n) p_{\text{eq}}(\mathbf{r}_n, t_n), \quad (4.2)$$

where $p_{\text{eq}}(\mathbf{r}_n, t_n)$ is the equilibrium probability density, $P(\mathbf{r}_{n-1}, t_{n-1} | \mathbf{r}_n, t_n)$ is a conditional probability density (cf. Paper I). The Boltzmann equilibrium distribution is given by

$$p_{\text{eq}}(\mathbf{r}, t) = p_{\text{eq}}(\mathbf{r}) \\ = \frac{\exp[-U(x, y, z)/kT]}{\int_0^{L_x} \int_0^{L_y} \int_0^{L_z} dx dy dz \exp[-U(x, y, z)/kT]}. \quad (4.3)$$

Here we are interested in just the stationary $p_{\text{eq}}(\mathbf{r})$ consistent with thermodynamic equilibrium for the many-body system. By substituting the variables, the normalization coefficient in Eq. (4.3) can be recast in the following way:

$$\int_0^{L_x} \int_0^{L_y} \int_0^{L_z} dx dy dz \exp[-U(x, y, z)/kT] \\ = V \int_0^1 \int_0^1 \int_0^1 d\xi d\eta d\zeta \exp[-U(L_x \xi, L_y \eta, L_z \zeta)/kT] \\ \equiv VI(L_x, L_y, L_z), \quad (4.4)$$

with $\xi \equiv x/L_x$, etc. Using the expression for the ensemble-averaged time-ordered exponential [Eq. (3.1) of Paper I] one can pull out the normalization integral from the ensemble averaging in Eq. (4.1) and write that

$$G(t) = (2^{-N} qN) O \left\{ 2 - \frac{1}{VI(L_x, L_y, L_z)} \right. \\ \times \left[\left\langle 1 - \exp_O \left[-i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle' \right. \\ \left. + \left\langle 1 - \exp_O \left[i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle' \right]^{N-1} \right\}, \quad (4.5)$$

where the prime indicates ensemble-averaging with respect to the unnormalized equilibrium distribution. By substituting for the volume, $V=N/C$, one can take the limit $N \rightarrow \infty$, so Eq. (4.5) becomes

$$G(t) = \lim_{N \rightarrow \infty} \frac{qN}{2} O \left\{ 1 - \frac{C}{2NI(\sqrt[3]{N/C})} \right. \\ \times \left[\left\langle 1 - \exp_O \left[-i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle' \right. \\ \left. + \left\langle 1 - \exp_O \left[i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle' \right]^{N-1} \right\}. \quad (4.6)$$

If the potential $U(\mathbf{r})$ vanishes at $|\mathbf{r}| \rightarrow \infty$, then the integral I of Eq. (4.6) approaches unity, and one obtains as a final result, in a manner analogous to the Markov method,^{10,17} that

$$G(t) = \frac{qN}{2} O \exp \left\{ -\frac{C}{2} \right. \\ \times \left[\left\langle 1 - \exp_O \left[-i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle' \right. \\ \left. + \left\langle 1 - \exp_O \left[i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle' \right] \right\}, \quad (4.7)$$

where we have used the fact¹⁸ that

$$\lim_{N \rightarrow \infty} \left[1 - \frac{f(N)}{N} \right]^N = e^{-\lim_{N \rightarrow \infty} f(N)}, \quad (4.8)$$

provided that the limit of $f(N)$ exists and is finite.

Equation (4.7) is still written in a rather symbolic manner which contains ensemble-averaged ordered exponentials. It can further be rewritten in the form

$$G(t) = \frac{qN}{2} \exp_O \left[C \int_0^t dt' \frac{\partial g(t')}{\partial t'} \right] \\ = \frac{qN}{2} \exp \left[C \int_0^t dt' \frac{\partial g(t')}{\partial t'} \right], \quad (4.9)$$

where $g(t) \equiv [g_+(t) + g_-(t)]/2$, and the individual spin isochromats are given by

$$g_{\pm}(t) = \left\langle \exp_O \left[\mp i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle' \\ = \left\langle \exp \left[\mp i \frac{3}{4} \chi \int_0^t dt' F(\mathbf{r}(t')) \right] \right\rangle'. \quad (4.10)$$

Correspondence between Eqs. (4.7) and (4.9) can be established by differentiating with respect to time the formal series solution given by Eq. (3.4) of Paper I. By comparing the expression for $G(t)$, Eq. (4.1) with its thermodynamic limit, Eq. (4.9), we have found that in the limit of a large number of particles the time ordering in $G(t)$ becomes unnecessary.

Note that $G(t)$ decays to 0 when $t \rightarrow \infty$, as it should, since it describes an FID signal. Indeed

$$\begin{aligned}
G(\infty) &= \exp \left[C \int_0^\infty dt' \frac{\partial g(t')}{\partial t'} \right] \\
&= \exp [C(-g(0) - i\omega \tilde{g}(\omega))|_{\omega=0}] \\
&= \exp [-Cg(0)], \quad (4.11)
\end{aligned}$$

where $\tilde{g}(\omega)$ is the Fourier transform of $g(t)$. But $g_\pm(0)$ is equal to the integral of the unnormalized Boltzmann equilibrium distribution over volume V , cf. Sec. III of Paper I, which yields at $N \rightarrow \infty$ and $V \rightarrow \infty$

$$\begin{aligned}
G(\infty) &= \lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty}} \exp [-Cg(0)] \\
&= \exp \left\{ -\frac{C}{2} [g_+(0) + g_-(0)] \right\} \\
&= \lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty}} \exp \left\{ -C \int d^3r \exp [-U(r)/kT] \right\} \\
&= \lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty}} \exp [-NI(\sqrt[3]{V})] = 0, \quad (4.12)
\end{aligned}$$

where the integral I is defined in Eq. (4.4). Equation (4.9) can be rewritten in terms of a differential equation for $G(t)$, viz.

$$\frac{\partial G(t)}{\partial t} = C \frac{\partial g(t)}{\partial t} G(t). \quad (4.13)$$

By performing the Fourier–Laplace transform of Eq. (4.13), one can write that

$$\begin{aligned}
i\omega \tilde{G}(\omega) - \frac{iC}{2\pi} \int_{-\infty}^{+\infty} (\omega - \omega') \tilde{g}(\omega - \omega') \tilde{G}(\omega') d\omega' \\
= [Cg(0) - 1]G(0). \quad (4.14)
\end{aligned}$$

Thus, it is sufficient to know just the two-spin line shape function $\tilde{g}(\omega)$ and the concentration C to solve for $\tilde{G}(\omega)$. Equation (4.14) can be transformed into a matrix equation by discretizing the convolution kernel with respect to ω and ω' , and then inverted numerically.

It is easy to see that the solution of Eq. (4.14) is expected to be close to a Lorentzian. First we note that the two-spin spectral function $\tilde{g}(\omega)$ is expected to be much narrower than the N -body $\tilde{G}(\omega)$, and therefore, it is not unreasonable to approximate it by an infinitesimally narrow Lorentzian, viz.

$$\tilde{g}(\omega - \omega') \approx g(0) \frac{\tau'}{1 - i(\omega - \omega')\tau'}, \quad \tau' \rightarrow \infty. \quad (4.15)$$

(Here we are ignoring the infinitesimal “Pake doublet” for simplicity.) Substituting Eq. (4.15) into Eq. (4.14) and using the identity $\int_{-\infty}^{+\infty} \tilde{G}(\omega') d\omega' = 2\pi G(0)$, we obtain

$$\begin{aligned}
i\omega \tilde{G}(\omega) - \frac{Cg(0)}{2\pi\tau'} \int_{-\infty}^{+\infty} \frac{\tau'}{1 - i(\omega - \omega')\tau'} \tilde{G}(\omega') d\omega' \\
\approx -G(0). \quad (4.16)
\end{aligned}$$

We can now consider the kernel of the integral equation as just a delta function, which yields

$$\tilde{G}(\omega) \approx \frac{G(0)}{[Cg(0)/\tau'] - i\omega}, \quad (4.17)$$

i.e., the many-body spectral function is given by a Lorentzian with half-width $Cg(0)/\tau'$, or in the absence of any potential $CV/\tau' = N/\tau'$, where $N \rightarrow \infty$ and $\tau' \rightarrow \infty$ (or $V \rightarrow \infty$ and $\tau' \rightarrow \infty$), cf. Eq. (4.10). Equation (4.17), of course, describes the line shape only qualitatively, since one still has to solve for τ' as a function of volume V and the diffusion coefficient D_T until one converges to the thermodynamic limit.

V. TREATMENT OF MULTIPLE PULSES USING THE EIGENOPERATOR BASIS: SOLID-ECHO SEQUENCE

In this section, we consider effects of multiple nonselective hard pulses applied to a many-body spin system. As an illustrative example, let us consider a solid echo experiment involving an intermediate $(\pi/2)_y$ pulse, viz.

$$\left(\frac{\pi}{2}\right)_x \xrightarrow{\tau} \left(\frac{\pi}{2}\right)_y \xrightarrow{t} \text{acquire}. \quad (5.1)$$

Immediately after the intermediate pulse, the density matrix in the rotating frame becomes

$$\rho(\tau+) = \sum_{\{\epsilon\}} g_{\{\epsilon\}}(\tau) R(\theta) E_{\{\epsilon\}} R^{-1}(\theta), \quad (5.2)$$

where $R(\theta)$ is the rotation operator. In the rotating frame, $R(\theta)$ is equal to $\exp(i\theta \Sigma_y^{(0)})$ with $\theta = \pi/2$ for the case of solid echo. In general, the rotation of an eigenoperator $E_{\{\epsilon\}}$ will yield a linear combination of the eigenoperators $E_{\{\epsilon'\}}$ that form a complete basis set

$$R(\theta) E_{\{\epsilon\}} R^{-1}(\theta) = \sum_{\{\epsilon'\}} X_{\{\epsilon\}\{\epsilon'\}} E_{\{\epsilon'\}}. \quad (5.3)$$

The elements of the pulse propagator matrix \mathbf{X}^T in the eigenoperator space can be defined as

$$\begin{aligned}
X_{\{\epsilon\}\{\epsilon'\}} &\equiv \text{Tr}[E_{\{\epsilon'\}}^\dagger R(\theta) E_{\{\epsilon\}} R^{-1}(\theta)] \\
&= \text{Tr}[E_{\{\epsilon\}} R^{-1}(\theta) E_{\{\epsilon'\}}^\dagger R(\theta)]. \quad (5.4)
\end{aligned}$$

To relate the components $g_{\{\epsilon\}}(t)$ before and immediately after the pulse, we write a new expansion for the density matrix $\rho(\tau+)$ in terms of the eigenoperators

$$\rho(\tau+) = \sum_{\{\epsilon\}} g_{\{\epsilon\}}(\tau+) E_{\{\epsilon\}}. \quad (5.5)$$

Comparing Eqs. (5.2) and (5.5) and making use of Eq. (5.3) we find the relation between the vector of coefficients $g(\tau+)$ and $g(\tau)$

$$g(\tau+) = \mathbf{X}g(\tau). \quad (5.6)$$

After the pulse, the vector of coefficients continues to evolve as given by Eq. (2.9) for each element, but with a time shift of $t - \tau+$ and with the initial conditions at $\tau+$ determined by Eq. (5.6). Therefore, the overall vector $g(t)$ in the rotating frame, at times $t > \tau+$ is given by

$$g(t) = \left\langle e^{-i\Delta\Omega(t-\tau)} e^{-i\chi \sum_{i_1 < j_1}^N C^{(i_1 j_1)} \int_{\tau}^t dt_1 F(\mathbf{r}_{i_1 j_1}(t_1))} \right. \\ \left. \times \mathbf{X} e^{-i\Delta\Omega\tau} e^{-i\chi \sum_{i_1 < j_1}^N C^{(i_1 j_1)} \int_0^{\tau} dt_1 F(\mathbf{r}_{i_1 j_1}(t_1))} \right\rangle g(0), \quad (5.7)$$

where $\Delta\Omega$ is the offset matrix. Note that in the above expression the pulse propagator \mathbf{X} in general may mix all blocks of the \mathbf{C} -matrix, including the components with different coherence indices μ as opposed to a pure free-induction decay. As will shortly be seen, a $\pi/2$ pulse results in mixing of the components with $\mu = \pm 1$. Now, the diagonal matrix $\Delta\Omega$ containing frequencies $\mu(\Omega - \omega_{\text{rf}})$ commutes with the block-diagonal matrix \mathbf{C} , since $\Delta\Omega$ is just a constant matrix for each μ th block of \mathbf{C} , and we can write that

$$g(t) = e^{-i\Delta\Omega(t-\tau)} \left\langle e^{-i\chi \sum_{i_1 < j_1}^N C^{(i_1 j_1)} \int_{\tau}^t dt_1 F(\mathbf{r}_{i_1 j_1}(t_1))} \right. \\ \left. \times e^{-i\chi \sum_{i_1 < j_1}^N \mathbf{X} C^{(i_1 j_1)} \mathbf{X}^{-1} \int_0^{\tau} dt_1 F(\mathbf{r}_{i_1 j_1}(t_1))} \right\rangle \mathbf{X} e^{-i\Delta\Omega\tau} g(0), \quad (5.8)$$

where the equivalence of Eq. (5.8) to Eq. (5.7) may be shown by expanding out the exponential operators.

VI. MULTIPLE PULSES: TIME ORDERING AND THE GENERALIZED CUMULANT EXPANSION

The next step is to perform the ensemble averaging of the ordered exponential of Eq. (5.8) by taking into account the statistical independence of the motions of spins, as has been done for the case of a pure FID. Using the standard procedure for constructing generalized cumulants,⁷ one obtains that

$$\left\langle \exp_O \left[-i\chi \sum_{i_1 < j_1}^N C^{(i_1 j_1)} \int_{\tau}^t dt_1 F(\mathbf{r}_{i_1 j_1}(t_1)) \right] \right. \\ \left. \times \exp_O \left[-i\chi \sum_{i_1 < j_1}^N \mathbf{X} C^{(i_1 j_1)} \mathbf{X}^{-1} \int_0^{\tau} dt_1 F(\mathbf{r}_{i_1 j_1}(t_1)) \right] \right\rangle \\ = \exp_O \left\langle \exp_O \left[-i\chi \sum_{i_1 < j_1}^N C^{(i_1 j_1)} \int_{\tau}^t dt_1 F(\mathbf{r}_{i_1 j_1}(t_1)) \right. \right. \\ \left. \left. + \mathbf{X} C^{(i_1 j_1)} \mathbf{X}^{-1} \int_0^{\tau} dt_1 F(\mathbf{r}_{i_1 j_1}(t_1)) \right] - 1 \right\rangle_c, \quad (6.1)$$

where c stands for the cumulant averaging. Note that the time ordering O also takes care of the fact that $C^{(i' j')}$ and $\mathbf{X} C^{(i'' j'')} \mathbf{X}^{-1}$ do not in general commute. Indeed, integrals of the type $\int_0^{\tau} dt'' \int_{\tau}^t dt'$ cannot be time-ordered since in this case $t' \geq t''$ everywhere, and thus $C^{(i' j')}$ can never be to the right of $\mathbf{X} C^{(i'' j'')} \mathbf{X}^{-1}$ after the ordering is performed for the second time. If the motions of spins are statistically independent, by expanding the second ordered exponential in Eq. (6.1), one obtains

$$\exp_O \sum_{n=1}^{\infty} (-i\chi)^n \sum_{p=0}^n \sum_{i_1 < j_1}^N \cdots \sum_{i_p < j_p}^N \sum_{i_{p+1} < j_{p+1}}^N \cdots \sum_{i_n < j_n}^N C^{(i_1 j_1)} \cdots C^{(i_p j_p)} \mathbf{X} C^{(i_{p+1} j_{p+1})} \cdots C^{(i_n j_n)} \mathbf{X}^{-1} \\ \times \int_{\tau}^t dt_1 \cdots \int_{\tau}^{t_{p-1}} dt_p \int_0^{\tau} dt_{p+1} \cdots \int_0^{t_{n-1}} dt_n \langle F(\mathbf{r}_{i_1 j_1}(t_1)) \cdots F(\mathbf{r}_{i_p j_p}(t_p)) F(\mathbf{r}_{i_{p+1} j_{p+1}}(t_{p+1})) \cdots F(\mathbf{r}_{i_n j_n}(t_n)) \rangle_c \\ = \exp_O \sum_{n=1}^{\infty} (-i\chi)^n \sum_{p=0}^n \sum_{i < j}^N [C^{(ij)}]^p \mathbf{X} [C^{(ij)}]^{n-p} \mathbf{X}^{-1} \\ \times \int_{\tau}^t dt_1 \cdots \int_{\tau}^{t_{p-1}} dt_p \int_0^{\tau} dt_{p+1} \cdots \int_0^{t_{n-1}} dt_n \langle F(\mathbf{r}(t_1)) \cdots F(\mathbf{r}(t_p)) F(\mathbf{r}(t_{p+1})) \cdots F(\mathbf{r}(t_n)) \rangle_c. \quad (6.2)$$

Using the ordering prescription, one can obtain the expansion of the ordered exponential up to various orders m . Restricting ourselves for illustrative purposes to $m=0,1,2$ one obtains from Eq. (6.2) that

$$\begin{aligned}
& \exp_0 \sum_{n=1}^{\infty} (-i\chi)^n \sum_{p=0}^n \sum_{i < j}^N [\mathbf{C}^{(ij)}]^p \mathbf{X} [\mathbf{C}^{(ij)}]^{n-p} \mathbf{X}^{-1} \int_{\tau}^t dt_1 \cdots \int_{\tau}^{t_{p-1}} dt_p \int_0^{\tau} dt_{p+1} \cdots \int_0^{t_{n-1}} dt_n \\
& \times \langle F(\mathbf{r}(t_1)) \cdots F(\mathbf{r}(t_p)) F(\mathbf{r}(t_{p+1})) \cdots F(\mathbf{r}(t_n)) \rangle_c \mathbf{X} \exp(-i\Delta\Omega\tau) \mathbf{g}(0) \\
& = \left\{ 1 + \sum_{n=1}^{\infty} (-i\chi)^n \sum_{p=0}^n \sum_{i < j}^N [\mathbf{C}^{(ij)}]^p \mathbf{X} [\mathbf{C}^{(ij)}]^{n-p} \mathbf{X}^{-1} \int_{\tau}^t dt_1 \cdots \int_{\tau}^{t_{p-1}} dt_p \int_0^{\tau} dt_{p+1} \cdots \right. \\
& \quad \int_0^{t_{n-1}} dt_n \langle F(\mathbf{r}(t_1)) \cdots F(\mathbf{r}(t_p)) F(\mathbf{r}(t_{p+1})) \cdots F(\mathbf{r}(t_n)) \rangle_c + \sum_{n'=1}^{\infty} \sum_{n=1}^{\infty} (-i\chi)^{n'} (-i\chi)^n \\
& \quad \times \sum_{p=0}^n \sum_{i' < j'}^N \sum_{i < j}^N [\mathbf{C}^{(i'j')}]^{n'} [\mathbf{C}^{(ij)}]^{n-p} \mathbf{X} [\mathbf{C}^{(ij)}]^p \mathbf{X}^{-1} \int_{\tau}^t dt'_1 \cdots \int_{\tau}^{t'_{n'-1}} dt'_{n'} \int_{\tau}^{t'_{n'}} dt_1 \cdots \int_{\tau}^{t_{n-p-1}} dt_{n-p} \int_0^{\tau} dt_{n-p+1} \cdots \\
& \quad \int_0^{t_{n-1}} dt_n \langle F(\mathbf{r}(t'_1)) \cdots F(\mathbf{r}(t'_{n'})) \rangle_c \langle F(\mathbf{r}(t_1)) \cdots F(\mathbf{r}(t_n)) \rangle_c + \sum_{n'=1}^{\infty} \sum_{n=1}^{\infty} (-i\chi)^{n'} (-i\chi)^n \sum_{p'=1}^{n'} \sum_{i' < j'}^N \sum_{i < j}^N [\mathbf{C}^{(i'j')}]^{n'-p'} \\
& \quad \times \mathbf{X} [\mathbf{C}^{(i'j')}]^{p'} [\mathbf{C}^{(ij)}]^{n-p} \mathbf{X}^{-1} \int_{\tau}^t dt'_1 \cdots \int_{\tau}^{t'_{n'-p'-1}} dt'_{n'-p'} \int_0^{\tau} dt'_{n'-p'+1} \cdots \int_0^{t'_{n'-1}} dt'_{n'} \int_0^{t_{n-1}} dt_1 \cdots \\
& \quad \left. \int_0^{t_{n-1}} dt_n \langle F(\mathbf{r}(t'_1)) \cdots F(\mathbf{r}(t'_{n'})) \rangle_c \langle F(\mathbf{r}(t_1)) \cdots F(\mathbf{r}(t_n)) \rangle_c + \cdots \right\} \mathbf{X} \exp(-i\Delta\Omega\tau) \mathbf{g}(0). \quad (6.3)
\end{aligned}$$

The consistency of the ordering application can be checked by letting $\mathbf{X}=\mathbf{1}$, which corresponds to a pure FID signal. In this case the previous time-ordered ensemble-averaged exponential, Eq. (3.6), is recovered. The latter essentially follows from applying the following integral identities:

$$\int_{\tau}^t dt' + \int_0^{\tau} dt' = \int_0^t dt', \quad (6.4a)$$

$$\begin{aligned}
& \int_{\tau}^t dt' \int_{\tau}^{t'} dt'' + \int_{\tau}^t dt' \int_0^{\tau} dt'' + \int_0^{\tau} dt' \int_0^{t'} dt'' \\
& = \int_0^t dt' \int_0^{t'} dt'', \quad (6.4b)
\end{aligned}$$

$$\begin{aligned}
& \int_{\tau}^t dt' \int_{\tau}^{t'} dt'' \int_{\tau}^{t''} dt''' + \int_{\tau}^t dt' \int_{\tau}^{t'} dt'' \int_0^{\tau} dt''' \\
& + \int_{\tau}^t dt' \int_0^{\tau} dt'' \int_0^{t''} dt''' + \int_0^{\tau} dt' \int_0^{t'} dt'' \int_0^{t''} dt''' \\
& = \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''', \quad (6.4c)
\end{aligned}$$

and so on.

In Appendix B it is shown that, for a nonselective hard pulse, each subpart of the starting vector-coefficient $\mathbf{g}_l(0)$ is an eigenvector of the matrix sum $\sum_{i < j} [\mathbf{C}^{(ij)}]^p \mathbf{X} [\mathbf{C}^{(ij)}]^{n-p}$, where l denotes the number of operators I_{α} in the corresponding eigenoperator subset $E_{\{\epsilon\}}^{(0,l)}$. That is to say

$$\begin{aligned}
& \sum_{i < j}^N [\mathbf{C}^{(ij)}]^p \mathbf{X} [\mathbf{C}^{(ij)}]^{n-p} \exp(-i\Delta\Omega\tau) \mathbf{g}_l(0) \\
& = \cos(\Delta\Omega\tau) [I(\frac{3}{4})^p (-\frac{3}{4})^{n-p} \\
& \quad + (N-1-l)(-\frac{3}{4})^p (\frac{3}{4})^{n-p}] \mathbf{g}_l(0) \\
& = \cos(\Delta\Omega\tau) (\frac{3}{4})^n [(-1)^{n-p} l + (-1)^p (N-1-l)] \mathbf{g}_l(0), \quad (6.5a)
\end{aligned}$$

$$\mathbf{X} \mathbf{g}(0) = \mathbf{g}(0). \quad (6.5b)$$

Validity of Eq. (6.5b) also follows from the fact that a pure oscillating signal, which has the initial magnetization along the y axis, is not affected by an intermediate pulse around the y axis in the rotating frame. We shall further consider the case when $\Delta\Omega=0$, i.e., when the system is exactly on resonance, and define the following integral operators:

$$I_1 \equiv (-i\frac{3}{4}\chi) \int_0^{\tau} dt_1, \quad I_2 \equiv (-i\frac{3}{4}\chi) \int_{\tau}^t dt_1, \quad (6.6a)$$

$$I \equiv (-i\frac{3}{4}\chi) \int_{\tau}^t dt_1 - (-i\frac{3}{4}\chi) \int_0^{\tau} dt_1 \equiv (-i\frac{3}{4}\chi) \int_0^t dt_1 s(t_1), \quad (6.6b)$$

where the s -function is defined as follows: $s(t)=+1$ if $t > \tau$ and $s(t)=-1$ if $0 < t < \tau$. The following short-hand notation is also introduced:

$$\begin{aligned}
& \{I\}^n \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c \\
& \equiv \frac{1}{n!} \left(-i \frac{3}{4} \chi \right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \\
& \quad \times s(t_1)s(t_2) \cdots s(t_n) \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c \\
& = \left(-i \frac{3}{4} \chi \right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \\
& \quad \times s(t_1)s(t_2) \cdots s(t_n) \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c, \quad (6.7)
\end{aligned}$$

which can be further rewritten as [compare also with Eqs. (6.4a)–(6.4c)]

$$\begin{aligned}
& \{I\}^n \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c \\
& = (-i \frac{3}{4} \chi)^n \sum_{p=0}^n \int_{\tau}^t dt_1 \cdots \int_{\tau}^{t_{p-1}} dt_p \int_0^{\tau} dt_{p+1} \cdots \\
& \quad \int_0^{t_{n-1}} dt_n (-1)^{n-p} \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c \\
& = O \sum_{p=0}^n \{I_2\}^{n-p} (-1)^p \{I_1\}^p \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c. \quad (6.8)
\end{aligned}$$

The ordered product of integral operators acting on various cumulant partitionings n_1, n_2, \dots, n_m can also be written symbolically as [cf. Eqs. (5.15a)–(5.15c)]

$$\begin{aligned}
& O\{I\}^{n_m} \cdots \{I\}^{n_2} \{I\}^{n_1} \\
& = O \prod_{i=1}^m \{I\}^{n_i} \\
& = \sum_{p=0}^{n_m + \cdots + n_2 + n_1} O\{I_2\}^{n_m + \cdots + n_2 + n_1 - p} (-1)^p \{I_1\}^p. \quad (6.9)
\end{aligned}$$

We shall now prove by mathematical induction that the m th term of the expansion, Eq. (6.3) can be factorized as

$$\begin{aligned}
& [l + (-1)^{n_m}(N-1-l)] \cdots [l + (-1)^{n_2}(N-1-l)] \\
& \quad \times [l + (-1)^{n_1}(N-1-l)] O\{I\}^{n_m} \cdots \{I\}^{n_2} \{I\}^{n_1} \\
& = O \prod_{i=1}^m [l + (-1)^{n_i}(N-1-l)] \{I\}^{n_i}, \quad (6.10)
\end{aligned}$$

from which the ordered cumulant exponential function can be recollected later.

The $m=0$ and $m=1$ terms are evident from the eigenvalue properties of the starting vector $\mathbf{g}_l(0)$. Applying the ordering for the $m+1$ th term of the expansion and operating on the starting vector $\mathbf{g}_l(0)$, and using its eigenvalue properties, we obtain

$$\begin{aligned}
& \sum_{n_{m+1}=1}^{\infty} \sum_{n_m=1}^{\infty} \cdots \sum_{n_2=1}^{\infty} \sum_{n_1=1}^{\infty} \left\{ [l + (-1)^{n_{m+1}}(N-1-l)] O\{I_2\}^{n_{m+1}} \prod_{i=1}^{N_m} [l + (-1)^{n_i}(N-1-l)] \{I\}^{n_i} \right. \\
& \quad \left. + \sum_{p=1}^{n_{m+1}} [(-1)^p l + (-1)^{n_{m+1}-p}(N-1-l)] O\{I_2\}^{n_{m+1}-p} \{I_1\}^p \prod_{i=1}^{N_m} [(-1)^{n_i} l + (N-1-l)] \{I\}^{n_i} \right\}, \quad (6.11)
\end{aligned}$$

where $N_m \equiv n_1 + n_2 + \cdots + n_m$. Substituting $p \rightarrow p - N_m$, in the second term and using the notation of Eq. (6.9), we can add up the two terms yielding

$$\begin{aligned}
& \sum_{n_{m+1}=1}^{\infty} \sum_{n_m=1}^{\infty} \cdots \sum_{n_2=1}^{\infty} \sum_{n_1=1}^{\infty} \left\{ \prod_{i=1}^{m+1} [l + (-1)^{n_i}(N-1-l)] O\{I_2\}^{n_{m+1}} \sum_{p=0}^{N_m} \{I_2\}^{N_{m+1}-p} (-1)^p \{I_1\}^p \right. \\
& \quad \left. + \sum_{p=N_m+1}^{n_{m+1}} [l(-1)^{p-N_m} + (-1)^{N_{m+1}-p}(N-1-l)] \prod_{i=1}^m [l(-1)^{n_i} + (N-1-l)] O\{I_2\}^{N_{m+1}-p} \{I_1\}^p \right\} \\
& = \prod_{i=1}^{m+1} [l + (-1)^{n_i}(N-1-l)] \sum_{p=0}^{N_{m+1}} O\{I_2\}^{N_{m+1}-p} (-1)^p \{I_1\}^p = O \prod_{i=1}^{m+1} [l + (-1)^{n_i}(N-1-l)] \{I\}^{n_i}, \quad (6.12)
\end{aligned}$$

which completes the proof by induction. Collecting back the ordered cumulant exponential function, we get

$$\begin{aligned}
& O \exp \sum_{n=1}^{\infty} [l + (-1)^n(N-1-l)] \{I\}^n \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c \\
& = \exp_O \sum_{n=1}^{\infty} (-i\chi)^n \left[\left(\frac{3}{4} \right)^n l + \left(-\frac{3}{4} \right)^n (N-1-l) \right] \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n s(t_1)s(t_2) \cdots s(t_n) \langle F(t_1)F(t_2) \cdots F(t_n) \rangle_c. \quad (6.13)
\end{aligned}$$

Thus, one can rewrite Eq. (5.7) in terms of usual ensemble-averaged exponentials by using Eq. (6.13)

$$\left\langle \exp_O \left[-i\chi \sum_{i_1 < j_1}^N C^{(i_1 j_1)} \int_{\tau}^t dt_1 F(\mathbf{r}_{i_1 j_1}(t_1)) \right] \right\rangle \exp_O \left[-i\chi \sum_{i_1 < j_1}^N C^{(i_1 j_1)} \int_0^{\tau} dt_1 F(\mathbf{r}_{i_1 j_1}(t_1)) \right] \Bigg| \mathbf{g}_I(0) = 0 \\ \times \left\langle \exp_O \left[-i\frac{3}{4}\chi \int_0^t dt_1 s(t_1) F(\mathbf{r}(t_1)) \right] \right\rangle^l \left\langle \exp_O \left[i\frac{3}{4}\chi \int_0^t dt_1 s(t_1) F(\mathbf{r}(t_1)) \right] \right\rangle^{N-1-l} \mathbf{g}_I(0). \quad (6.14)$$

Summing over the components $g_{\{e\}}^{(0,l)}(t)$ having total statistical weight of $N(N-1)$, Eq. (3.4), one can finally rewrite the observed solid-echo signal in the rotating frame on resonance

$$G(t) = (2^{-N} q N) O \left\langle \exp_O \left[-i\frac{3}{4}\chi \int_0^t dt' s(t') F(\mathbf{r}(t')) \right] + \exp_O \left[i\frac{3}{4}\chi \int_0^t dt' s(t') F(\mathbf{r}(t')) \right] \right\rangle^{N-1}, \quad (6.15)$$

i.e., a binomial expression is again obtained, as in the case of a pure many-body FID signal, Eq. (4.1). The latter is easily obtained from Eq. (6.15) by setting $s(t)=1$ everywhere. However, the derivation of Eq. (6.15) could be also regarded as a formal check of the consistency of the introduced time-ordering “ O ” for treating the ensemble averaging of exponential operators, which in general do not commute but are applied during different periods of time, i.e., one is from 0 to τ and the other is from τ to t .

Equation (6.15) can be extended to the limit of a large number of particles exactly in the same way as it was done for the FID signal by using the Markov method. Taking the limit $N \rightarrow \infty$, $V \rightarrow \infty$ yields

$$G(t) = \frac{qN}{2} \exp \left\{ -\frac{C}{2} \right. \\ \times \left[\left\langle 1 - \exp_O \left[-i\frac{3}{4}\chi \int_0^t dt' s(t') F(\mathbf{r}(t')) \right] \right\rangle' \right. \\ \left. + \left\langle 1 - \exp_O \left[i\frac{3}{4}\chi \int_0^t dt' s(t') F(\mathbf{r}(t')) \right] \right\rangle' \right] \Bigg\}, \quad (6.16)$$

which is to be compared with Eq. (4.7). The ensemble-averaged exponentials are evaluated by solving the appropriate modified stochastic Liouville equation taking into account the s -function as described in Paper I [cf. Eqs. (4.9) and (4.10) of Paper I].

For very slow motions, i.e., as $D_T \rightarrow 0$, in averaging the exponentials in Eqs. (6.15) and (6.16) we can hope to approximate the two-spin stochastic Liouville operator as $L_{\pm} \approx -1/\tau'' \pm i\frac{3}{4}\chi F(\mathbf{r})$, where τ'' is an effective diffusional relaxation time with $\tau''^{-1} \propto D_T^{\alpha}$, (cf. Fig. 5 of Paper I where $\alpha=1/2$). (However, more generally we can expect τ'' to depend on the value of τ and \mathbf{r} , cf. Ref. 19 for related cases.) In this limit, the homogeneous line broadening is expected to be much less than the inhomogeneous line broadening. The solid-echo signal could then be written approximately as

$$G(t) \propto \frac{qN}{2} \exp \left(-\frac{N}{\tau''} t \right) \exp \left(-\frac{|t-2\tau|}{T_2^*} \right). \quad (6.17)$$

Here the inhomogeneous $T_2^{*-1} = R_2^*$ is given in the thermodynamic limit by the Anderson formula, cf. Sec. III, and the

ratio N/τ'' may be regarded as a homogeneous relaxation rate, T_2^{-1} in the limit $N \rightarrow \infty$ and $\tau'' \rightarrow \infty$. In Eq. (6.17), the inhomogeneous line broadening gets refocused, whereas the homogeneous line broadening yields the decay of the echo amplitude. From the behavior of the echo signal described

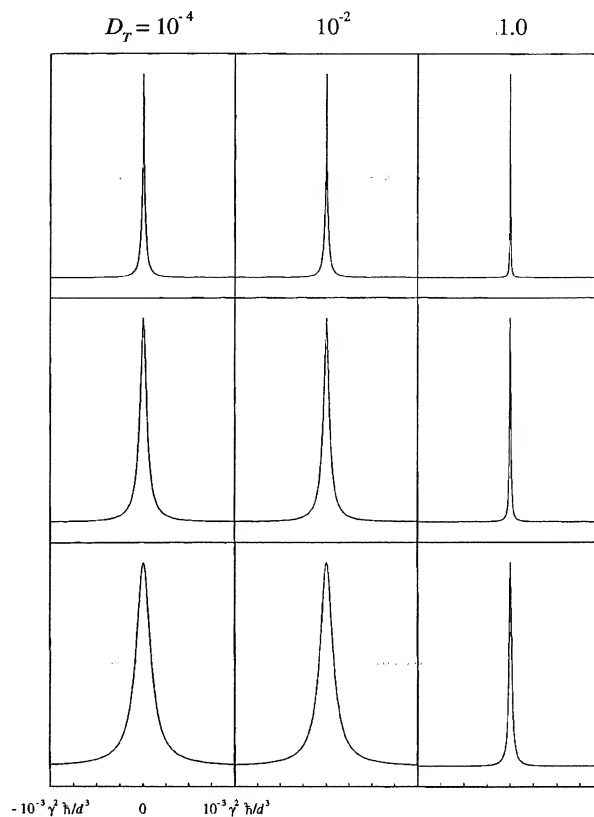


FIG. 1. Many-body line shapes for spins of 1/2 in the thermodynamic limit as a function of the diffusion coefficient, D_T (in units of $\gamma^2 \hbar/d^3$), and concentration of spins, C of 1.2, 2.4, and 4 (in units of 10^{16} cm^{-3}) from top down. The values for C and D_T are as indicated. The ratio r_{max}/d was set to 100, after checking that this led to convergent results; then C was varied by varying the number of spins, N . Concentrations were calculated from $C = N/V$, where $V = (4\pi/3)r_{\text{max}}^3$, where d was arbitrarily set to 10 Å. Line shapes are close to Lorentzians over the entire motional range for all concentrations considered. Increasing the concentration of spins yields a proportional increase in spectral linewidths; whereas increasing the diffusion rate D_T results in motional narrowing.

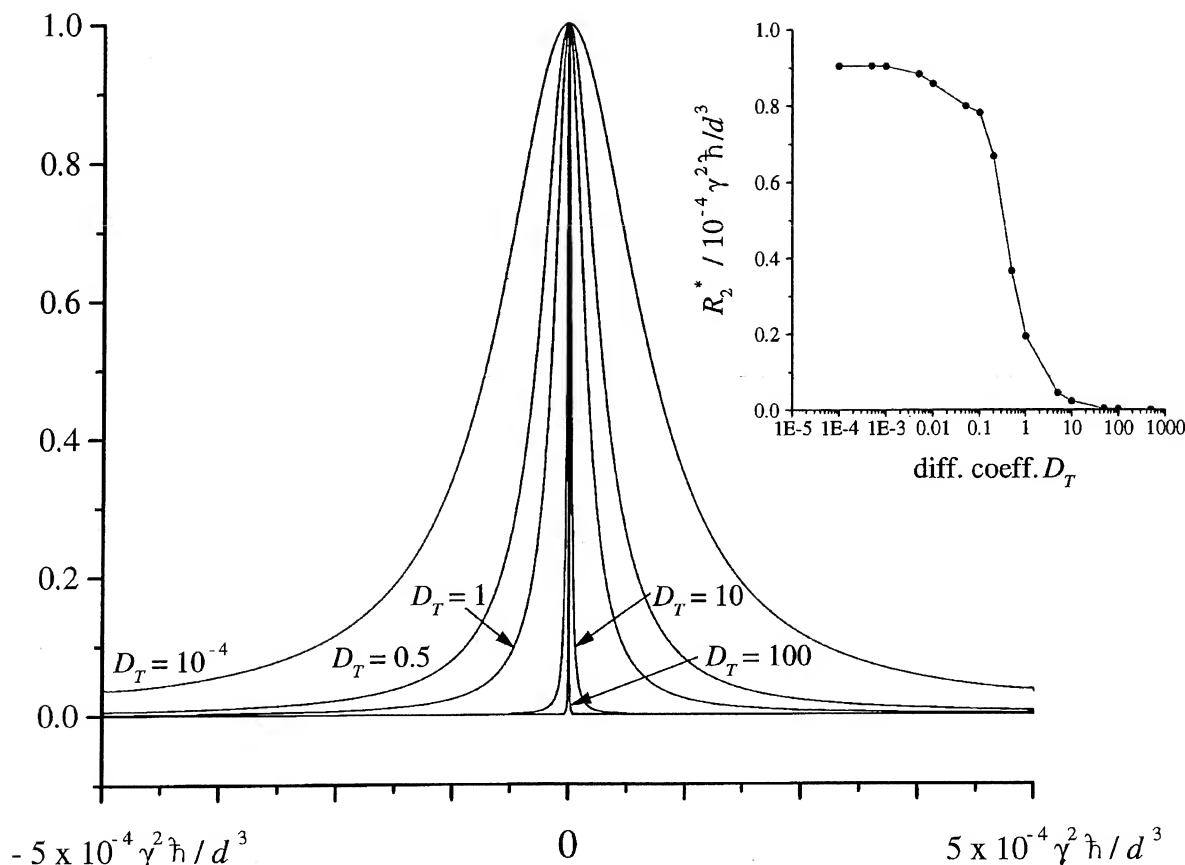


FIG. 2. Line shapes and spectral linewidths, R_2^* (inset) in the thermodynamic limit as a function of the diffusion coefficient D_T calculated for the concentration of spins $C=2.4 \times 10^{16} \text{ cm}^{-3}$ with $d=10 \text{ \AA}$. Line shapes have been fit to a Lorentzian function, from which the line broadening term, R_2^* , has been determined. The plot of R_2^* vs D_T (inset) shows the behavior of linewidths over the whole motional range considered.

qualitatively by Eq. (6.17), one can see that even in the limit of very slow motions, one can expect a decay of the echo amplitude in a multiple-spin system, i.e., the many-body echo may not be refocused completely at 2τ . However, below we shall only use the more general expression, Eq. (6.16) without assuming any simplified limiting form of the type of Eq. (6.17). We shall indeed find that the above simple argument has some qualitative validity, but more quantitatively T_2^{-1} is given by a fractional power law somewhat different from $D_T^{1/2}$.

VII. SIMULATIONS OF MANY-BODY SPECTRAL LINE SHAPES AND ECHOES IN THE PRESENCE OF TRANSLATIONAL DIFFUSION

Figure 1 shows the line shapes in the thermodynamic limit associated with a large number of particles allowed to diffuse in a large volume. The ensemble-averaged ordered exponentials have been calculated by the stochastic Liouville equation method (cf. Paper I). Convergence of the spectra has been checked by increasing the number of particles, N and the ratio r_{max}/d , while keeping the concentration, C constant. [Here we may use dimensionless units for C , i.e., $C = N/V$, where $V = (4\pi/3)(r_{\text{max}}/d)^3$]. It was found that if the number of particles N is more than 100, then an r_{max}/d of about 100 is sufficient to obtain a converged line shape. One

also needs to discretize the convolution kernel of Eq. (4.14) with 4000 frequency points. Interestingly, the r_{max}/d required for convergence was not found to depend appreciably on D_T , implying that the significant volume of spins surrounding a test spin remains the same, independent of motional rate. Line shapes are very close to Lorentzians over the motional rates considered. This was checked by fitting them to Lorentzian functions (see below). Increasing the concentration yields a proportional increase in widths.

To further explore the many-body line shape function, spectral linewidths were calculated as a function of the diffusion coefficient at a fixed concentration, and are shown in Fig. 2 ($C=2.4 \times 10^{16} \text{ cm}^{-3}$, $d=10 \text{ \AA}$). The linewidths were determined by nonlinear least-square fits of the line shapes to a Lorentzian function. As can be seen from Fig. 3 plotted on a semilogarithmic scale (inset), the curve has the form of a sigmoidal function with a characteristic point of transition to the “quasi-solid state” limit at a value of the diffusion coefficient D_T of ~ 0.05 (in units of $\gamma^2 \hbar / d$). For electron spin-bearing molecules for which the distance of closest approach between their centers is $d=10 \text{ \AA}$, this value of D_T converts to $1.64 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is typical for spin labels in moderately viscous liquids (e.g., liquid crystals²⁰). For $C=2.4 \times 10^{16} \text{ cm}^{-3}$ one has a value of R_2^* of $2.61 \times 10^4 \text{ s}^{-1}$. One would need higher concentrations to obtain an observ-

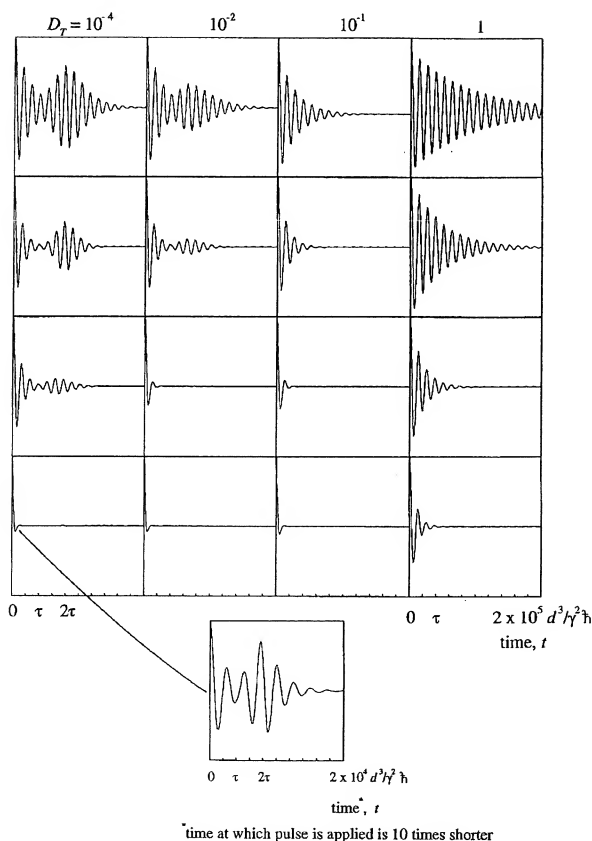


FIG. 3. Simulation of the solid echoes for N spins of $1/2$ in the thermodynamic limit as a function of diffusion coefficient D_T (in units of $\gamma^2 \hbar / d$) and concentration of spins, C , of 2.4, 4.8, 12, 24 (in units of 10^{16} cm^{-3}) from top down, at exact resonance. As C increases, the signal decays faster, yielding no echo at higher concentrations. However, by decreasing the time τ , at which the second pulse is applied, one recovers the echo again (cf. inset). The abscissa is in units of time from 0 to $2 \times 10^5 d^3 / \gamma^2 \hbar$; inset from 0 to $2 \times 10^4 d^3 / \gamma^2 \hbar$.

able effect. Thus, increasing C by a factor of 200 ($8 \times 10^{-3} \text{ M}$) yields an R_2^* of $5.22 \times 10^6 \text{ s}^{-1}$, which should be measurable.²¹ In the case of proton NMR (nuclear magnetic resonance), D_T of 0.05 translates into $3.78 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. This would mean that slow motional effects set in only for extremely slow motions characteristic of high-molecular weight polymers or diffusion in solids.

Figure 3 shows many-body solid echoes at exact resonance. The distance of minimum approach has been taken to be $d = 10 \text{ \AA}$. For illustrative purposes only, we have included a nonzero carrier frequency. Increasing the concentration of spins yields a decrease in the echo amplitude. Thus, going from $C = 2.4 \times 10^{16} \text{ cm}^{-3}$ to $C = 2.4 \times 10^{17} \text{ cm}^{-3}$ results in almost no detectable echo signal in the latter case even in the very slow motional regime ($D_T = 10^{-4}$). Increasing the diffusion rate also yields a decrease in the echo amplitude, so that it becomes impossible to refocus the dipolar interaction for faster motions. This happens for smaller D_T as C gets larger. Refocusing of the echo at larger C can still be achieved by applying the second $(\pi/2)_y$ pulse much earlier. For instance, we find that in order to get an appreciable refocusing of the echo signal near the rigid limit, for a concen-

tration of electron spins of $C = 5 \times 10^{18} \text{ cm}^{-3}$ (or $\sim 8 \times 10^{-3} \text{ M}$), the second pulse must be applied no later than 600 ns after the first pulse (not shown), which is easily achieved by pulsed ESR methods. However, this should be regarded only as a rough estimate, since in the present analysis additional factors leading to a loss of refocusing (e.g., additional homogeneous line broadening, noise, etc.), have not been taken into account.

The above effect of concentration on the refocusing of the echo is illustrated in Fig. 4. Here the echo envelopes, i.e., intensities measured vs $t_1 = 2\tau$, are plotted at various concentrations ranging from $C = 2.4 \times 10^{16} \text{ cm}^{-3}$ to $2.4 \times 10^{18} \text{ cm}^{-3}$ ($d = 10 \text{ \AA}$). As can be seen, at high C the decay of the echo envelope is much faster, thus resulting in no echo at sufficiently long τ 's. (The actual procedure we used was to calculate the SECSY signal, then Fourier transform it with respect to t_2 , and then to study the t_1 dependence of the $\omega_2 = 0$ slice, cf. Paper I, Sec. V.)

Figure 5 shows the homogeneous relaxation times T_2 as a function of the diffusion coefficient D_T plotted for different concentrations of spins C . The T_2 values have been obtained by fitting the echo envelopes (cf. Fig. 4) to single exponential functions. This method of determining T_2 's corresponds to the SECSY technique as described in Paper I [cf. Fig. 4(a) and its discussion in that paper]. The data in Fig. 5 have been rescaled with respect to concentration, so that a departure from linear dependence on concentration (of about 10%) can be seen. This occurs in the slow motional regime, which also shows a limiting dependence on the diffusion rate that goes as $D_T^{-0.32}$ (vs the $D_T^{-0.5}$ dependence found for a two-spin case in Fig. 5 of Paper I). By contrast, in the motional narrowing regime homogeneous relaxation times depend linearly on both the concentration, C and D_T . Note that increasing C does not shift the T_2 minimum. In addition, the T_2 minimum for a system of multiple spins is shallower than that for a two-spin system (cf. Fig. 5 of Paper I).

Finally, a comparison of the spectral linewidths, R_2^* , with the decay rate of the echo envelope, R_2 , is shown in Fig. 6 ($C = 2.4 \times 10^{16} \text{ cm}^{-3}$, $d = 10 \text{ \AA}$). Here the log-log scale has been used to show the solid-state limit, the intermediate region, and the motional-narrowing limit. In the fast motional limit (larger D_T values), line broadening is fully homogeneous, and R_2 approaches R_2^* . The curve then becomes linear with a slope of -1 which corresponds to the motional-narrowing, or Redfield limit as given by Eq. (3.12). The intermediate motional limit occurs near the position of the R_2 minimum, i.e., $\sim D_T = 0.05$, and spans about two orders of magnitude in D_T . As $D_T \rightarrow 0$, R_2^* values approach the limiting Anderson expression for linewidths given by Eq. (3.15), whereas R_2 further decreases with D_T . Thus, in the slow motional limit there is a clear separation between R_2^* , which mostly consists of inhomogeneous line broadening, and R_2 , which may be regarded as homogeneous line broadening. Note that at $D_T = 0.05$, $R_2 \approx R_2^*$; thus, for the above example of electron spins with $C \approx 8 \times 10^{-3} \text{ M}$, R_2 would be about $5 \times 10^6 \text{ s}^{-1}$, which can be a significant contribution to the homogeneous linewidth.¹⁹

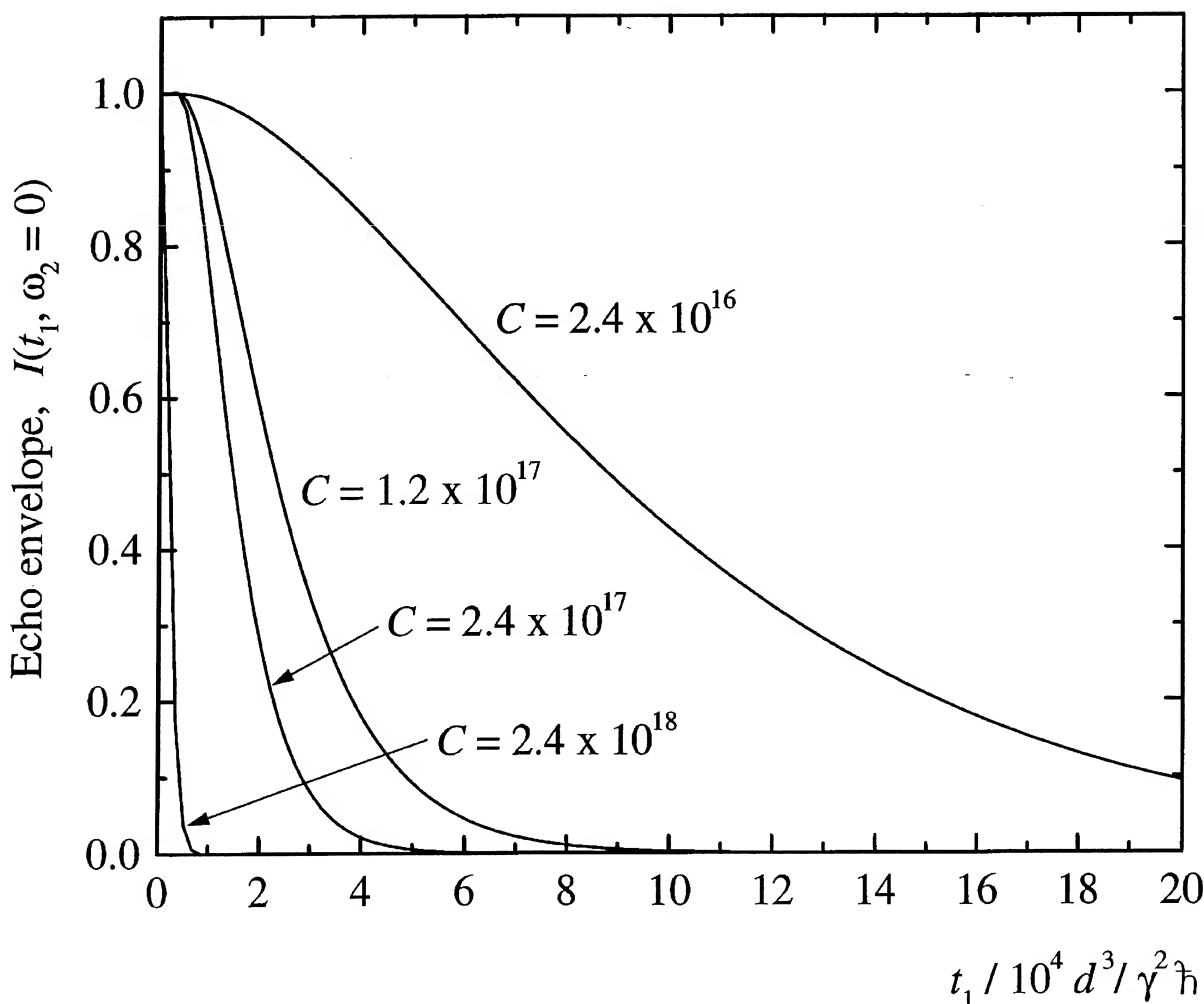


FIG. 4. Effect of concentration on echo refocusing. Here the echo envelopes are calculated at various concentrations as indicated for a very slow motional rate ($D_T = 10^{-4} \gamma^2 \hbar / d$). The intensities are measured from a SECSY simulation [cf. Paper I, Fig. 4(a)] that is Fourier transformed just with respect to t_2 . Then the slices at $\omega_2 = 0$ were plotted as a function of the delay time $t_1 = 2\tau$. Increasing concentration results in no echo at sufficiently long τ 's.

VIII. SUMMARY AND CONCLUSIONS

The main result in this work is the solution for the magnetic resonance line shape arising from N identical particles that bear spins of $1/2$ and are undergoing dipolar interactions which are modulated by their relative translational motion. This result describes the whole motional range from the rigid limit through the motional narrowing regime. The general result for the FID, Eq. (4.1), only required the assumption of the stochastic independence of the motions of the spins and the usual high temperature approximation, Eq. (3.3). Equation (4.1) shows that the many-body solution for N identical spins of $1/2$ may be obtained from just a knowledge of the behavior of a single pair of particles, and it is written as a time-ordered binomial expression involving the two-spin isochromats associated with the two allowed transitions resulting from the interacting pair of spins of $1/2$. In the very slow motional limit, the line shape expression yields Anderson's statistical theory for line shapes in a rigid lattice. In the motional narrowing regime it is consistent with the well-known Torrey results. In the thermodynamic limit, i.e., when N

$\rightarrow \infty$ and $V \rightarrow \infty$, under the assumption of a stationary process (i.e., a system at equilibrium), a simple integral equation, Eq. (4.14), has been obtained for the many-body line shape function, $\tilde{G}(\omega)$ in terms of the two-spin line shape function $\tilde{g}(\omega)$ and the concentration, $C = N/V$.

The general expression for the many-body FID signal, Eq. (3.11) was generalized to the proto-typical solid echo pulse sequence, Eq. (6.15), and then to the thermodynamic limit, Eq. (6.16). The solution was rigorously developed for the case of exact resonance. This case guarantees that no new orders of coherence besides ± 1 are produced by nonselective pulses in a system of N identical spins of $1/2$. (This follows rigorously from the eigenvalue properties of the starting vector and the interaction matrices in the eigenoperator representation.) This result also depends on the high-temperature approximation for the equilibrium density matrix, as well as the assumption of the statistical independence of the motions of the spins. Removing either of these assumptions would result in generating other orders of coherence, as is well-known in solid-state NMR.²²

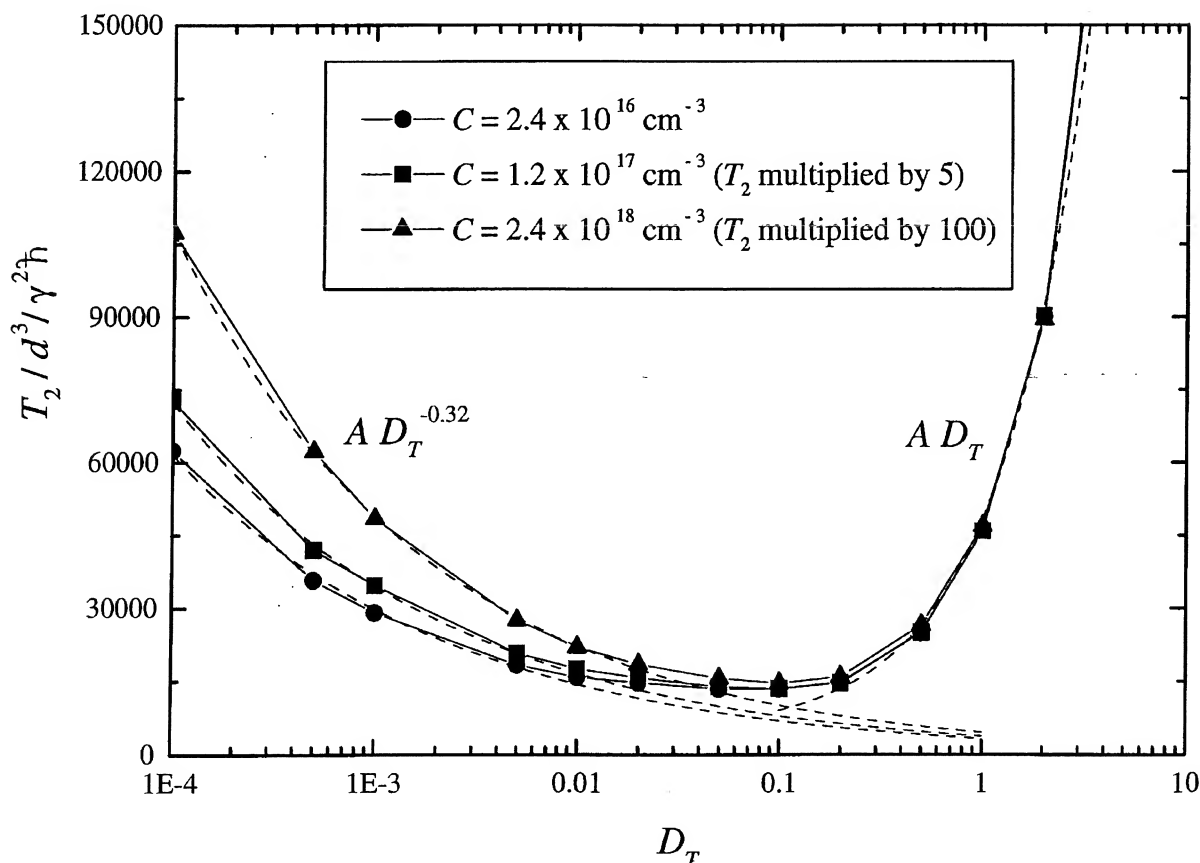


FIG. 5. Homogeneous relaxation times, T_2 , for N spins of $1/2$ in the thermodynamic limit as a function of the diffusion coefficient D_T , calculated for three different concentrations as indicated. The values at the higher concentration were rescaled accordingly in order to illustrate the departure from the linear dependence of T_2 on D_T , as opposed to T_2^* . A T_2 minimum is seen at $\sim D_T = 0.05 \gamma^2 \hbar / d$, i.e., at about the same value as for the case of two spins of $1/2$, cf. Fig. 4 of Paper I. However, for multiple spins, the T_2 minimum is shallower. Dashed lines show fits to limiting power-law behavior of T_2 on D_T in the slow and fast motional limits.

Convergent calculations of the many-body line shapes and echoes could readily be performed based on the stochastic Liouville equation for two spin-bearing particles undergoing simple Brownian relative translational diffusion. These calculations showed that a Lorentzian line, whose width is proportional to C , is obtained over the whole motional range and is in agreement with the Anderson solid-state limit and the Redfield motional narrowing limit. The solid echo simulations show characteristic echoes for very slow motions, which are attenuated as the motional rate increases and/or C becomes larger. In particular, the homogeneous T_2 's, which are associated with the echo decay show a power-law dependence in the very slow motional regime (as $D_T^{-0.32}$). Although some departure from a linear dependence of T_2^{-1} on C is found at slow motions (unlike the case for T_2^{*-1}), similar values are found for the D_T 's that correspond to the T_2 minima.

The present work may thus be seen as a unifying method which bridges limiting theories of many-body magnetic resonance developed about four decades ago. The generalized cumulant method has proven to be a powerful tool for finding ensemble-averaged FID or solid echo components in the case when motions of the spin-bearing particles are uncorre-

lated. In addition, the expansion of the density matrix in the set of symmetry-adapted eigenoperators allows one to take full advantage of the inherent symmetries of the problem, such as those associated with the statistical independence of the motions of spins and with the nonselectivity of pulses for like spins.

We believe that the method of representing the commutation superoperator in an eigenoperator space may be extended to more complex problems, including the relaxation of unlike spins and more involved pulse sequences. Among the advantages of this method are: more transparent symmetry properties of the interaction matrix and relatively simple vector-matrix multiplications involved. Moreover, it may allow one to treat more complicated forms of the spin Hamiltonian, such as for spins greater than $1/2$. In subsequent work we intend to further explore the formal properties of the many-body interaction Hamiltonian in the eigenoperator representation for the purpose of developing a methodology for treating multiple quantum coherences and cases of unlike spins.

The results in the present paper can best be studied in dilute solutions of like spins of $1/2$, where the dipolar interaction is significant, and the slow motional regime may be

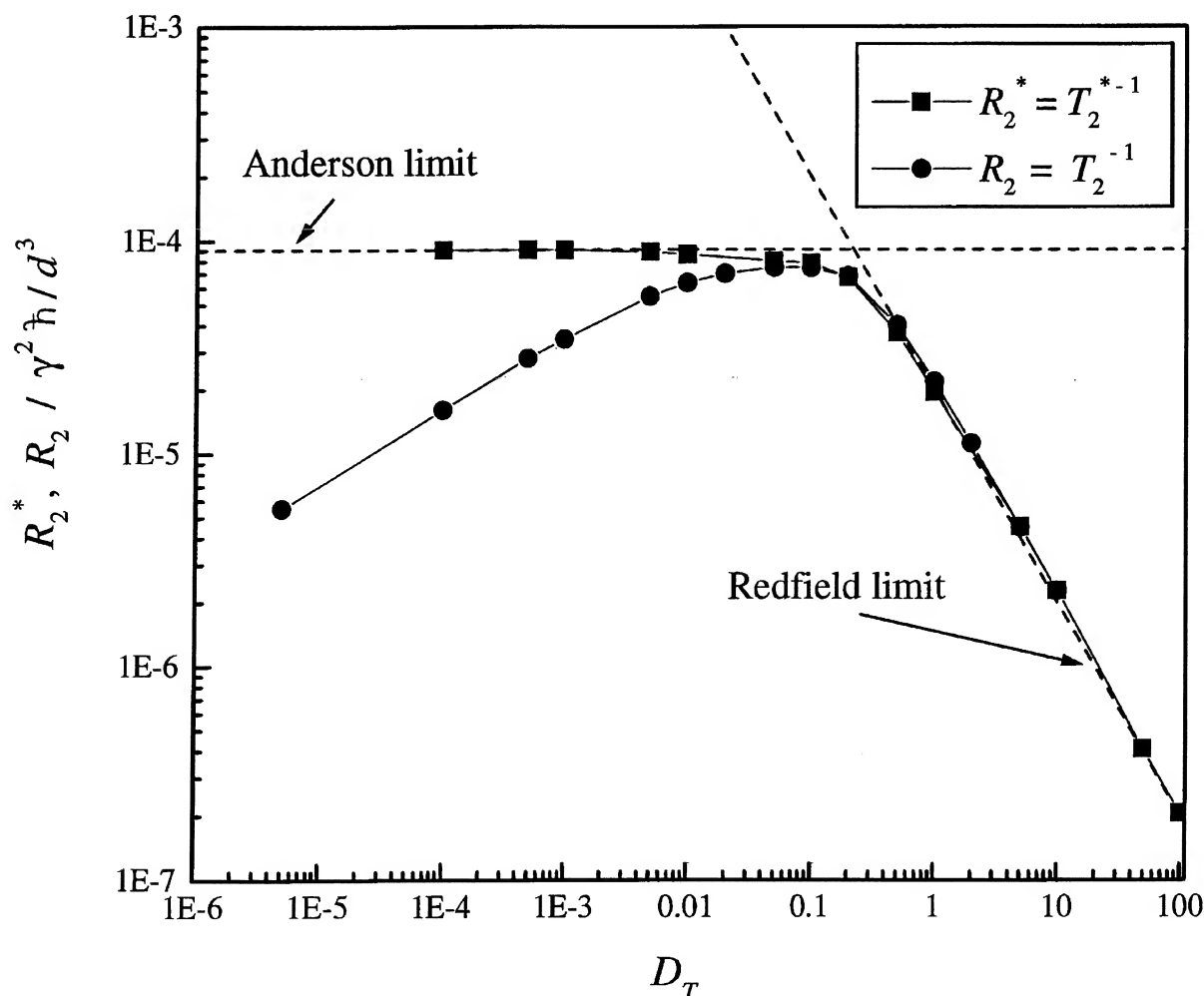


FIG. 6. Comparison of homogeneous and total broadening (R_2 and R_2^* , respectively) for multiple spins as a function of the diffusion coefficient D_T , plotted on a logarithmic scale showing the solid state limit, the motional narrowing limit, and the intermediate motional region. Dashed lines indicate R_2^* calculated using Eqs. (3.12) and (3.15) for the Redfield (fast motional) limit and the Anderson (solid-state) limit, respectively. The R_2 maximum occurs in the intermediate motional region; whereas in the motional narrowing limit R_2^* and R_2 approach each other.

conveniently achieved. This would be the case for ESR studies on radicals, where slow motional effects set in even for moderately viscous fluids. Given the weak power dependence of $D_T^{-0.32}$ for the homogeneous T_2 in the viscous (or slow motional) regime, this contribution would persist over a wide range of viscosities. An additional matter for study is the practical case of a complex spin Hamiltonian that includes hyperfine couplings of the electron spin on each radical to the magnetic nuclei, when present. This will require generalization of our approach to more complex spin Hamiltonians along the lines suggested in the previous paragraph. Finally we note that only intermolecular spin interactions including intermolecular dipolar and (Heisenberg) spin exchange terms require a many-body approach; intramolecular spin interactions, that are usually modulated just by rotational tumbling, can be more simply treated by the effective two-body stochastic motional analyses of Paper I and references therein.

ACKNOWLEDGMENTS

We wish to thank Dr. Peter P. Borbat, Dr. Keith A. Earle, and Dr. David J. Schneider, and Professor David B. Zax for insightful discussions. This work was supported by grants from the NSF and the NIH.

APPENDIX A: EIGENVALUES OF THE MATRIX SUMS, $\sum_{i,j}^N [C_i^{(i,j)}]^n$

The first important observation we shall make is that the right-hand side of Eq. (3.6) for $g_i(t)$ is invariant under a permutation of any two particles. On the other hand, permuting the two particles will at most switch two components of the left-hand sub-vector of coefficients $g_i(t)$ that have the same indices k and m . Making as many pairwise permutations as necessary, one can then show that $g_{\epsilon}^{(k,m)}(t) = g_{\epsilon'}^{(k,m)}(t)$ for all ϵ and ϵ' . In fact this is independent of whatever numbering system that is chosen to number the

permutation sets $\{\epsilon\}$. Therefore, it is sufficient to calculate only a single component of $\mathbf{g}_\epsilon(t)$, i.e., $g_\epsilon^{(k,m)}(t)$.

Let us now consider the l th block of the matrix $\mathbf{C}_l^{(i,j)}$ defined in Eq. (2.10) and compute the result of the action of the matrix on the initial magnetization sub-vector, $\mathbf{g}_l(0)$. For a given spin pair (i,j) one can schematically represent the individual blocks of the matrix $\mathbf{C}_l^{(i,j)}$ according to the classification scheme for the coefficients $g_{\{\epsilon\}}^{(k,m)}(t)$, cf. discussion below Eq. (2.16) noting that only coefficients $g_\epsilon^{(k,m)}(t)$ and $g_{\epsilon'}^{(k \mp 1, m \pm 1)}(t)$ are coupled by $\mathbf{C}_l^{(i,j)}$. Indices k and m will then vary from 0 to $N-1-l$ and from l to $2l-N+1$, respectively. One can represent the product $\mathbf{C}_l^{(i,j)}\mathbf{g}_l(0)$ in the following form:

$$\mathbf{C}_l^{(i,j)}\mathbf{g}_l(0) = \begin{array}{c} \begin{array}{|c|c|c|c|} \hline (k,m) & & & \\ \hline (0,l) & & & \\ \hline & (1,l-1) & & \\ \hline & & (2,l-2) & \\ \hline & & & (3,l-3) \\ \hline & & & \dots \\ \hline & & & \vdots \\ \hline & & & \dots \\ \hline \end{array} & \times & \begin{array}{|c|} \hline 1 \\ \hline 0 \\ \hline 0 \\ \hline 0 \\ \hline \dots \\ \hline \end{array} \end{array} \quad (\text{A1})$$

Here the nonzero elements of the matrix $\mathbf{C}_l^{(i,j)}$ are contained within the squares. Clearly, the result of the multiplication with blocks having $k \geq 2$ will yield zeroes identically. Therefore, it is just necessary to discuss the blocks with $k=0$ and 1.

In Eq. (A1) the diagonal block with $k=0$ will reflect couplings amongst operators of the same type, $I_+ I_\alpha I_\alpha \dots I_\alpha I_\beta I_\beta \dots I_\beta$, which contain exactly one operator I_+ , $m=l$ operators I_α , and $N-1-l$ operators I_β corresponding to the different spins. As follows from the commutation relations, cf. Eqs. (2.11), the block with $k=0$ contains $2(N-1)$ nonzero rows, which correspond to twice the number of distinct pairs that one can form with the operators I_+ and the remaining $(N-1)$ operators I_α and I_β . For a given spin pair (i,j) , each nonzero row of the block will contain exactly two numbers, $\pm 1/2$ and $\pm 1/4$, where the plus sign corresponds to the operation on $I_+^{(i)} I_\alpha^{(j)}$ or $I_+^{(j)} I_\alpha^{(i)}$ and a minus sign to the operation on $I_+^{(i)} I_\beta^{(j)}$ or $I_+^{(j)} I_\beta^{(i)}$. Let us denote the positions of these two nonzero numbers (ϵ, ϵ') and (ϵ, ϵ') , respectively, where ϵ is the index of the original coefficient $g_\epsilon^{(k,m)}(t)$ and ϵ' is the index of the coefficient $g_{\epsilon'}^{(k,m)}(t)$ that is obtained by switching of particles i and j . Now, the lower left off-diagonal (i.e., the $[(0,l), (1,l)]$ block in Eq. (A1) will reflect couplings between operators of two different types, namely, $I_+ I_\alpha I_\alpha \dots I_\alpha I_\beta I_\beta \dots I_\beta$ and $I_+ I_\alpha I_\alpha \dots I_\alpha I_\beta I_\beta \dots I_\beta$. The operators of the former type having $k=1$ can be numbered by its own prescription $\{\delta\}$. According to the commutation relations, each nonzero row of the off-diagonal block, e.g., rows δ and δ' , will contain one $+1/4$ term and one $-1/4$

term which will cancel each other upon multiplying by a column vector of all ones. Therefore, the result of action of the matrix $\mathbf{C}_l^{(i,j)}$ on the initial magnetization vector $\mathbf{g}_l(0)$ is,

$$\begin{array}{|c|c|} \hline \begin{array}{c} (\pm \frac{1}{2})_{\epsilon\epsilon} \dots (\pm \frac{1}{4})_{\epsilon\epsilon'} \\ \vdots \\ (\pm \frac{1}{4})_{\delta'\epsilon} \dots (\pm \frac{1}{2})_{\delta'\epsilon'} \end{array} & \begin{array}{c} \vdots \\ \vdots \\ \vdots \end{array} \\ \hline \end{array} \times \begin{array}{|c|} \hline 1 \\ \hline 1 \\ \hline 1 \\ \hline 1 \\ \hline 1 \\ \hline 1 \\ \hline 1 \\ \hline 0 \\ \hline 0 \\ \hline 0 \\ \hline \dots \\ \hline 0 \\ \hline \end{array} = \begin{array}{|c|} \hline (\pm \frac{3}{4})_\epsilon \\ \hline \vdots \\ \hline (\pm \frac{3}{4})_{\epsilon'} \\ \hline \vdots \\ \hline (0)_{\delta} \\ \hline \vdots \\ \hline (0)_{\delta'} \\ \hline \end{array} \quad (\text{A2})$$

In order to compute $[\mathbf{C}_l^{(i,j)}]^2 \mathbf{g}_l(0)$, we note that the columns of the lower off-diagonal block containing nonzero elements will always correspond to zero rows of the diagonal block of $\mathbf{C}_l^{(i,j)}$ with $k=0$ [denoted as ϵ'' and ϵ''' in Eq. (A2)]. Indeed, as follows from the commutation relations, operators having $k=1$ are obtained from operators with $k=0$ when the combinations $I_\alpha^{(i)} I_\beta^{(j)}$ or $I_\alpha^{(j)} I_\beta^{(i)}$ are encountered, which cannot arise in the upper diagonal block describing the couplings between operators containing combinations $I_+^{(i)} I_\alpha^{(j)}$ and $I_+^{(j)} I_\alpha^{(i)}$ [or $I_+^{(i)} I_\alpha^{(j)}$ and $I_+^{(j)} I_\beta^{(i)}$]. Therefore, when multiplied by the matrix $\mathbf{C}_l^{(i,j)}$ for the second time, the lower half of the resulting vector corresponding to $k \neq 0$ will still consist of zeroes, since nonzero elements in rows δ or δ' of the lower off-diagonal blocks will be multiplied by zeroes at positions ϵ'' and ϵ''' arising from the previous action of the matrix $\mathbf{C}_l^{(i,j)}$. This means that the spin-flip terms in the dipolar Hamiltonian like $I_+^{(i)} I_-^{(j)}$, apart from a numerical factor of $3/4$ in the interaction constant, do not affect the observable FID signal after a single nonselective $\pi/2$ pulse. By contrast, the ϵ th (or ϵ' th) component of $\mathbf{g}_l(0)$ with $k=0$ will become $(\pm 3/4)^2$. Repeating this operation n times and summing over all spin pairs containing $m=l$ pairwise combinations $I_+^{(i)} I_\alpha^{(j)}$ each yielding one $(3/4)^n$, and $(N-1-m)$ combinations $I_+^{(i)} I_\beta^{(j)}$ yielding one $(-3/4)^n$, one obtains for any ϵ that

$$\left\{ \sum_{\epsilon} [\mathbf{C}_l^{(i,j)}]^n \mathbf{g}_l(0) \right\}_\epsilon = [l(\frac{3}{4})^n + (N-1-l)(-\frac{3}{4})^n]. \quad (\text{A3})$$

Applying the permutation symmetry argument given in the first paragraph of this Appendix, we conclude that $\mathbf{g}_l(0)$ is an eigenvector of the matrix sums $\sum_{i < j} [\mathbf{C}_l^{(i,j)}]^n$, with an eigenvalue given by Eq. (A3).

APPENDIX B: EIGENVALUES OF THE MATRIX SUMS, $\sum_{i < j}^N [\mathbf{C}_i^{(i,j)}]^p \mathbf{X} [\mathbf{C}_j^{(i,j)}]^{n-p}$

We shall now prove that for a nonselective or hard pulse, each sub-vector of the starting vector $\mathbf{g}_i(0)$ is an eigenvector of the matrix sum $\sum_{i < j}^N [\mathbf{C}_i^{(i,j)}]^p \mathbf{X} [\mathbf{C}_j^{(i,j)}]^{n-p}$, where l denotes

$$\begin{aligned} [I_+^{(i_1)} I_\alpha^{(i_2)} \dots I_\beta^{(i_3)} \dots I_+^{(i_4)} I_-^{(i_5)} \dots]_{(-\pi/2)_y} &= 2^{-N} (-I_\alpha^{(i_1)} + I_\beta^{(i_1)} + I_+^{(i_1)} - I_-^{(i_1)}) \\ &\times \underbrace{(I_\alpha^{(i_2)} + I_\beta^{(i_2)} + I_+^{(i_2)} + I_-^{(i_2)}) \dots (I_\alpha^{(i_3)} + I_\beta^{(i_3)} - I_+^{(i_3)} - I_-^{(i_3)}) \dots}_{m \text{ terms}} \\ &\times \underbrace{(-I_\alpha^{(i_4)} + I_\beta^{(i_4)} + I_+^{(i_4)} - I_-^{(i_4)}) (-I_\alpha^{(i_5)} + I_\beta^{(i_5)} - I_+^{(i_5)} + I_-^{(i_5)}) \dots}_{2k \text{ terms}}, \end{aligned} \quad (\text{B1})$$

with an analogous expression for eigenoperators having $\mu = -1$. Note that the signs of both the transformation to the rotating frame and the rotations by the pulse have been reversed here to get directly the elements of matrix \mathbf{X} , and not of its transpose, cf. Eq. (5.3). As can be seen from Eq. (B1), a $(\pi/2)_y$ pulse mixes, in principle, all the components of the vector-coefficient $\mathbf{g}(t)$ with different coherence indices, μ . However, in the high-temperature approximation, cf. Eq. (3.3), only the elements of the starting vector $\mathbf{g}(0)$ corresponding to $k=0$ are nonzero, and, for the initial magnetization after the first $\pi/2$ pulse along the x axis, are equal (apart from the factor of $2^{-N} \hbar \Omega / 2i k T$) to either $+1$ for $\mu = +1$, or -1 for $\mu = -1$, which significantly simplifies the calculation. According to Eq. (B1), individual products containing spins i and j will yield the following combinations after the second pulse:

$$[I_+^{(i)} I_\alpha^{(j)}]_{(-\pi/2)_y} \rightarrow \begin{cases} \pm I_\pm^{(i)} I_\alpha^{(j)} & \text{and } \pm I_\pm^{(i)} I_\beta^{(j)} \\ -I_\pm^{(j)} I_\alpha^{(i)} & \text{and } I_\pm^{(j)} I_\beta^{(i)}, \end{cases} \quad (\text{B2a})$$

$$[I_+^{(i)} I_\beta^{(j)}]_{(-\pi/2)_y} \rightarrow \begin{cases} \pm I_\pm^{(i)} I_\alpha^{(j)} & \text{and } \pm I_\pm^{(i)} I_\beta^{(j)} \\ I_\pm^{(j)} I_\alpha^{(i)} & \text{and } -I_\pm^{(j)} I_\beta^{(i)}, \end{cases} \quad (\text{B2b})$$

$$[I_\alpha^{(i)} I_\beta^{(j)}]_{(-\pi/2)_y} \rightarrow \begin{cases} I_\pm^{(i)} I_\alpha^{(j)} & \text{and } I_\pm^{(i)} I_\beta^{(j)} \\ -I_\pm^{(j)} I_\alpha^{(i)} & \text{and } -I_\pm^{(j)} I_\beta^{(i)}, \end{cases} \quad (\text{B2c})$$

$$[I_+^{(i)} I_-^{(j)}]_{(-\pi/2)_y} \rightarrow \begin{cases} \mp I_\pm^{(i)} I_\alpha^{(j)} & \text{and } \pm I_\pm^{(i)} I_\beta^{(j)} \\ \pm I_\pm^{(j)} I_\alpha^{(i)} & \text{and } \mp I_\pm^{(j)} I_\beta^{(i)}. \end{cases} \quad (\text{B2d})$$

Other combinations containing $I_\pm^{(i)} I_\pm^{(j)}$, $I_\alpha^{(i)} I_\alpha^{(j)}$, and $I_\beta^{(i)} I_\beta^{(j)}$ will yield zeroes upon further multiplication by the matrices $[\mathbf{C}^{(i,j)}]^p$ as follows from the commutation relations, Eq. (2.11), and, therefore, can be disregarded. The result of the matrix multiplication of the initial vector $\mathbf{g}(0)$ by matrices $[\mathbf{C}^{(i,j)}]^{n-p}$ is discussed in detail in Appendix A. In particular, for given k and m the vector $[\mathbf{C}^{(i,j)}]^{n-p} \mathbf{g}(0)$ contains the

the number of operators I_α in an eigenoperator subset $E_{\{\epsilon\}}^{(0,l)}$ having zero pairs $I_+ I_-$, i.e., $k=0$.

As a result of a single nonselective $-\pi/2$ pulse around the y axis applied at time τ , the eigenoperators $E_{\{\epsilon\}}^{(k,m)}$ corresponding to $\mu=1$ will transform in the rotating frame as follows:

same values at positions corresponding to the permutations of the two spins (i,j) and (j,i) , i.e., $(\pm 3/4)^{n-p}$. When the vector $[\mathbf{C}^{(i,j)}]^{n-p} \mathbf{g}(0)$ is further multiplied by \mathbf{X} , for the positions in the resulting vector that correspond to combinations containing $I_+^{(i)} I_\alpha^{(j)}$, the matrix multiplication over coefficients at $I_+^{(i)} I_\alpha^{(j)}$ and $I_+^{(j)} I_\alpha^{(i)}$ will yield zeroes; whereas the sums over positions corresponding to $I_+^{(i)} I_\beta^{(j)}$ or $I_+^{(j)} I_\beta^{(i)}$ of $[\mathbf{C}^{(i,j)}]^{n-p} \mathbf{g}(0)$ will be doubled. By contrast, for positions of the resulting vector pertaining to $I_+^{(i)} I_\beta^{(j)}$, the sums over positions having $I_+^{(i)} I_\beta^{(j)}$ or $I_+^{(j)} I_\beta^{(i)}$ will vanish, while the sums over pairs $I_+^{(i)} I_\alpha^{(j)}$ and $I_+^{(j)} I_\alpha^{(i)}$ will double. As can also be seen from Eqs. (B2c) and (B2d), the matrix multiplication over positions corresponding to $I_\alpha^{(i)} I_\beta^{(j)}$ or $I_\alpha^{(j)} I_\beta^{(i)}$ of the vector $[\mathbf{C}^{(i,j)}]^{n-p} \mathbf{g}(0)$ will always yield zeros. Therefore, for a given spin pair (i,j) the result of action of the matrix \mathbf{X} on vector $[\mathbf{C}^{(i,j)}]^{n-p} \mathbf{g}(0)$ will be just an exchange of values $(-3/4)^{n-p}$ and $(+3/4)^{n-p}$ at the nonzero positions of the vector $[\mathbf{C}^{(i,j)}]^{n-p} \mathbf{g}(0)$. These values need to be further weighted by twice the sum over all permutations for the remaining $N-2$ spins, including the sign of each permutation with which it appears in Eq. (B1). But this sum is formally just the sum over the coefficients of the polynomial represented in Eq. (B1), which can be readily obtained from Eq. (B1) by letting all the remaining $N-2$ polarization operators I_α and I_β equal to unity and the remaining lowering and raising operators I_+ and I_- to be all zeros. Thus, for $k=0$ this sum is equal to $2 \times 2^{-N} \times 2^{N-2} = 1/2$ and is zero for $k \neq 0$. Summing over the contributions from the components corresponding to both $\mu = +1$, having an additional factor of $\exp(-i\Delta\Omega\tau)$, and to $\mu = -1$ with $\exp(i\Delta\Omega\tau)$, and invoking the permutation symmetry arguments similar to those used earlier to find eigenvalues of the matrix sum $\sum_{i < j}^N [\mathbf{C}_i^{(i,j)}]^n$, cf. Appendix A, one has for the l th block of the coefficients $g_{\{\epsilon\}}^{(k,m)}(t)$ that

$$\begin{aligned}
& \sum_{i < j}^N [C_i^{(i,j)}]^p X[C_i^{(i,j)}]^{n-p} \exp(-i\Delta\Omega\tau) \mathbf{g}_i(0) \\
& = \cos(\Delta\Omega\tau) [I(\frac{3}{4})^p (-\frac{3}{4})^{n-p} \\
& \quad + (N-1-l)(-\frac{3}{4})^p (\frac{3}{4})^{n-p}] \mathbf{g}_l(0). \quad (\text{B3})
\end{aligned}$$

As can be seen from Eq. (B3), it includes a factor of $\cos(\Delta\Omega\tau)$ which diminishes the amplitude of the echo signal detected at the first-order coherence, since the remaining part of the signal is distributed amongst higher-order coherences. In this case, full forms of the matrices $C^{(i,j)}$, X , and $\Delta\Omega$ must be considered in order to derive Eq. (B3) rigorously, which will be a subject of the next paper.

¹H. C. Torrey, Phys. Rev. **92**, 962 (1953).

²A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

³L. P. Hwang and J. H. Freed, J. Chem. Phys. **63**, 4017 (1975).

⁴J. R. Klauder and P. W. Anderson, Phys. Rev. **125**, 912 (1962).

⁵A. M. Stoneham, Rev. Mod. Phys. **41**, 82 (1969); D. L. Orth, R. J. Mashl, and J. L. Skinner, J. Phys.: Condens. Matter **5**, 2533 (1993).

⁶A. A. Nevzorov and J. H. Freed, J. Chem. Phys. **112**, 1413 (2000), preceding paper.

⁷R. Kubo, J. Phys. Soc. Jpn. **17**, 1100 (1962).

⁸J. H. Freed, J. Chem. Phys. **49**, 376 (1968).

⁹J. H. Freed, in *Electron Spin Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), pp. 165–191.

¹⁰S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943).

¹¹J. Jeener, A. Vlassenbroek, and P. Broekaert, J. Chem. Phys. **103**, 1309 (1995).

¹²S. Lee, W. Richter, S. Vathyam, and W. S. Warren, J. Chem. Phys. **105**, 874 (1996).

¹³R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford University Press, Oxford, 1987).

¹⁴C. N. Banwell and H. Primas, Mol. Phys. **6**, 225 (1963).

¹⁵R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, edited by D. ter Haar (Oliver and Boyd, London, 1962), pp. 23–68.

¹⁶P. W. Anderson, Phys. Rev. **82**, 342 (1951).

¹⁷K. M. Salikhov and Yu. D. Tsvetkov, in *Time-domain Electron Spin Resonance*, edited by L. Kevan and R. N. Schwartz (Wiley, New York, 1979), pp. 231–277.

¹⁸I. N. Bronshtein and K. A. Semendyayev, *Handbook of Mathematics*, 3rd ed. (Springer, Berlin, 1997).

¹⁹L. J. Schwartz, A. E. Stillman, and J. H. Freed, J. Chem. Phys. **77**, 5410 (1982).

²⁰C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed. (Springer-Verlag, Heidelberg, 1990).

²¹J. K. Moscicki, Y.-K. Shin, and J. H. Freed, J. Chem. Phys. **99**, 634 (1993).

²²J. S. Hwang, R. P. Mason, L. P. Hwang, and J. H. Freed, J. Phys. Chem. **79**, 489 (1975).